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the treated fabric-covered rubber results in a relief design, with the ridges held up by foam rubber and the depressed areas of the fabric secured to the collapsed foam rubber. J. A. Woodruff
Text. Research J. June 1948

Elastic Fabric

Method of manufacturing elastic fabrics. Thomas H. Hawley, Jr., and Nicolai Timenes (to U. S. Rubber Co.). U.S. 2,434,111 (Jan. 6, 1948).

Drawings are shown of pin tenter machines and a coating device. The combination of these machines is used to make elastic fabrics by the successive steps of uniformly gathering up at least 15% of the normal length of the opposite edges of a textile fabric in relatively small gathers, uniformly stretching said fabric transversely to and between said edges by gradual increments until the fabric has been contracted in an amount substantially equal to the degree said edges were gathered and rendering said fabric elastic by adhesively uniting an elastic layer of rubber-containing material while said fabric is in the stretched condition. J. A. Woodruff
Text. Research J. June 1948

Plastic Imitation Fabric

Imitation fabric. Hugo Wurzburger (to Paul D. Wurzburger). U.S. 2,434,532 (Jan. 13, 1948).

A flexible nonwoven fabric simulating a conventional woven fabric composed of synthetic organic plastic material is formed by having the warp and filling filaments crossing in substantially the same plane. To offset rigidity incident to an imitation fabric of this type and to impart flexibility, one or more grooves extending at least $\frac{1}{3}$ of the way around the filaments are provided at the crossing points of the filaments. Modifications for various applications are described.
Text. Research J. June 1948 L. A. Fiori

Plastic Imitation Yarns

Imitation filaments, ropes, yarns, and the like. Hugo Wurzburger (to Paul D. Wurzburger). U.S. 2,434,533 (Jan. 13, 1948).

Provision is made, by means of special shaping rolls, auxiliary orifices, orifice rings, and other specially constructed devices, all of which work in conjunction with the regular extrusion orifice identified with synthetic organic plastic materials to provide a single filament to simulate the appearance of ordinary spun or twisted textile filaments, cords, or ropes. To impart flexibility, a helical groove is formed in its outer surface, where it extends from end to end of the filament according to a predetermined pitch. Several variations involving a series of grooves, shapes, and combinations of the two are given. L. A. Fiori
Text. Research J. June 1948

Printing Textiles

Process of printing textiles with a powdered blanket. William C. Ross (to Dewey & Almy Chemical Co.). U.S. 2,434,013 (Jan. 6, 1948).

An improved process of printing with an endless waterproof blanket is given. After the washing of the blanket, provision is made for the application of a dry powder to the surface of the blanket. The powder is said to make the removal of printing pastes from the blanket easier, as well as to eliminate the necessity of drying the blanket by heat.
J. A. Woodruff
Text. Research J. June 1948

Protective Clothing

Protective clothing. Henry C. Bazett and Paul A. Siple. U.S. 2,433,834 (Jan. 6, 1948).

A laminated garment for protection of the body against both dry and damp or wet, cold weather, comprising in combination (1) an absorbent inner lining layer of cotton or wool, (2) a second layer secured to the inner layer and consisting of any material, such as rubber vinylite, synthetic rubbers, or plastics, impermeable to both water and water vapor, (3) a third layer attached to the second layer and having a high thermal insulating value, such as wool, and (4) a moisture-impermeable layer similar to that which was used for the second layer. These layers of material may be stitched or cemented together.
Text. Research J. June 1948 L. A. Fiori

Rayon Treatment

Solvent for rayon and rayon treating solution. Charles L. Mantell (to United Merchants & Manufacturers, Inc.). U.S. 2,434,621 (Jan. 13, 1948).

A solvent for regenerated cellulose rayons is prepared by adding approximately 10% urea and 4.5% zinc oxide to an aqueous 10% solution of an alkali metal hydroxide, preferably sodium hydroxide. The viscosity and clarity of the solutions of rayon products dissolved in this solvent are said to be improved over solutions obtained with sodium zincate alone as the solvent. The use of the solvent is suggested for removing cellulose finishes from textile materials. The rayon solutions can also be used as textile finishes. J. A. Woodruff
Text. Research J. June 1948

Nonslip Rug

Nonslip textile article. Russell R. Matthews. U.S. 2,434,709 (Jan. 20, 1948).

A nonslip substance, such as a water dispersion of rubber, is applied only on the floor contact portion of the ribs of woven fabric normally used for rugs. Treatment consists of passing the rug over 2 rollers, 1 roller being partially immersed in a trough containing the nonslip liquid and having a peripheral speed slightly greater than the other roller. As the roll surfaces and the carpet slip with respect to each other, the ribs wipe the coating off without depositing any of it between the ribs. Air jets rupture any film or web of the coating which may accidentally extend from one rib to another. Claim is made that the coating, which has its greatest thickness at the line of contact of each ridge with the floor, improves the clinging ability of the rug. L. A. Fiori
Text. Research J. June 1948

TEXTILE RESEARCH JOURNAL

VOL. XVIII, No. 7 July, 1948

In This Issue

Cellulose Studies
X. Heterogeneous Degradation of Cellulose and Viscose Rayon in Organic Acid Solutions
P. C. Mehta and Eugene Pacsu 387

Imparting Water-Repellency to Textiles by Chemical Methods: A Review of the Literature
H. A. Schuyten, J. David Reid, J. W. Weaver, and John G. Frick, Jr. 396

Taber Yarn-Sheet Abrasion Test
E. M. Hicks and A. G. Scroggie 416

Constitutional Factors in the Production of Artificial Protein Fiber
Sam R. Hoover, Elsie L. Kokes, and Robert F. Peterson 423

An Application of Spectrophotometry in the Textile Industry: Testing Dyestuff Shipments
E. P. Mersereau and J. L. Barach 436

Book Reviews 440

Abstracts 442

Editor: Julian S. Jacobs *Managing Editor:* Julia M. Crisp

Associate Editors

H. J. Ball, Earl E. Berkley, Henry Eyring, Gustavus J. Esselen, Earl K. Fischer, Milton Harris, K. L. Hertel, H. Mark, E. R. Schwarz, Kyle Ward, Jr.

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TEXTILE RESEARCH JOURNAL

VOL. XVIII, No. 7 July, 1948

Cellulose Studies

X. Heterogeneous Degradation of Cellulose and Viscose Rayon in Organic Acid Solutions*

P. C. Mehta and Eugene Pacsu

Contribution from the Textile Foundation and Frick Chemical Laboratory, Princeton University

Abstract

On the basis of their experiments, Pacsu and Hiller have shown that the classical concept of the structure of cellulose as built up from glucose anhydride residues connected by 1,4-β-glycosidic linkages is inadequate. They proposed that in cellulose there are units of about 260 glucose anhydride residues linked through 1,4-β-glycosidic bonds, these units being then connected by hemiacetal or acetal bonds. The present experiments on the kinetics of heterogeneous hydrolysis of cellulose, in organic and inorganic acids, were conducted to test the validity of this concept. The results are: (1) an initial rapid hydrolysis down to a D.P. of about 260; $k = 3.43 \times 10^{-3}$ at 97° C, which is of a much higher order than the rate constant for hydrolysis of the 1,4-β-glycosidic bonds under similar conditions; (2) a practically complete standstill of the hydrolysis after the limiting D.P. of 260 is reached; (3) a negative value for the entropy of activation as calculated from Eyring's equation for absolute reaction rates, in contrast to the positive value obtained for the random hydrolysis of cellulose, starch, maltose, etc.

Similar experiments on commercial viscose rayon showed hydrolysis to be at a uniform rate down to a D.P. of about 60, after which no appreciable change occurred.

Introduction

It has been shown in Part IX [7] of this series that the present concept of cellulose postulating a linear macromolecule of about 3,000 to 3,500 β-D-glucopyranose residues uniformly connected through 1,4-glycosidic linkages is inadequate to explain satisfactorily the behavior of cellulose toward mild hydrolyzing agents. In earlier experiments (Part VIII) [5] it was found that the initial viscosity of a solution of surgical cotton in 85-percent phosphoric acid diminished rapidly with time and reached very low values. On the other hand, end-group analyses by the potassium permanganate method showed (Part VIII, Table III and Figure 5) that the rate of hydrolysis of the 1,4-glycosidic bonds in phos-

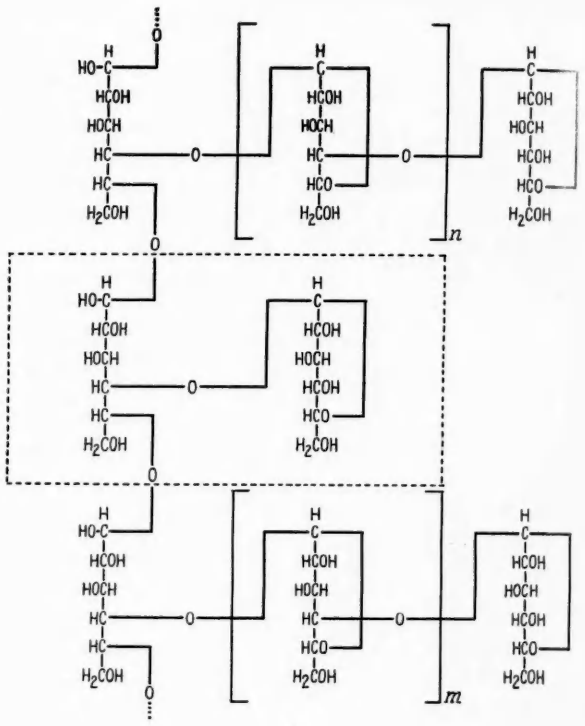
*The first paper in this series appeared in the October, 1945, issue. Papers II–VIII were published in March, April, June, July, August, October, and November, 1946, and Paper IX appeared in the August, 1947, issue.

Part of the work reported in this communication was sponsored by the Office of The Quartermaster General, Research and Development Branch, Contract W44-109-QM-1177.

phoric acid solution was extremely slow. From the rapid rate of the initial viscosity change it was calculated that cellulose in 85-percent phosphoric acid should hydrolyze into pure *D*-glucose in about 4 days. However, polarimetric measurements indicated that glucose formation did not take place even after several weeks, although the viscosity of the solution during that period had reached practically the same value as was shown by the solvent. Extensive rupture of 1,4-glycosidic bonds cannot, therefore, be involved in the formation of hydrocelluloses and in the rapid decrease in viscosity. On the basis of these results and other observations a new formula (I) has been proposed for cellulose in which long molecular chains are held together by hemiacetal linkages originating from open-chain glucose anhydride residues or glucose, cellobiose, cellotriose, etc., molecules.

A study of the rate of heterogeneous degradation of cellulose by dilute acids should provide a test for the correctness of the above picture. If the classical concept of cellulose structure is correct—that is, if only 1,4-glycosidic bonds are present in the cellulose molecule—then the hydrolysis should be random and the curve showing the degree of polymerization against length of treatment with acid should resemble the theoretical curve for random hydrolysis. Also, the calculated rate of the heterogeneous degradation should be comparable to the values given in the literature for the rate of hydrolysis of 1,4-glycosidic bonds. On the other hand, if the new concept is correct, the hydrolysis curve should consist of two distinct portions: the initial portion, in which the acid-sensitive hemiacetal bonds are being rapidly hydrolyzed, followed by another one in which there is a much slower hydrolysis of 1,4-glycosidic bonds. Furthermore, by making the conditions of hydrolysis mild enough so that the hydrolysis of 1,4-glycosidic bonds is negligible or extremely slow, it should be possible to get a sharp break in the hydrolysis curve after the initial cleavage of the hemiacetal bonds is completed. In other words, it should be possible to hydrolyze cellulose to a "limit hydrocellulose," after which the acid treatment should have a negligible effect. In our present experiments, we have attempted to obtain these conditions, and, as the results given later will show, we have been fairly successful in approximating these ideal conditions.

A review of the literature on hydrolysis of cellulose by acids reveals that most of the previous work



(I)

has been done under conditions sufficiently drastic to dissolve the cellulose. Thus, Willstätter and Zechmeister [11] followed the course of hydrolysis of cellulose in 41-percent hydrochloric acid, using the polarimetric method. Sherrard and Froehlke [9] subjected celluloses isolated from various woods to similar concentrations of acid. Freudenberg [4] used strong sulfuric acid and employed the iodine titration and the polarimetric methods to follow the hydrolysis. The mercaptalation method was used by Wolfrom and coworkers [12], who dissolved cotton linters in highly concentrated hydrochloric acid.

As stated before, we were interested in very mild hydrolysis of cellulose, and did not wish to exceed the stage when cellulose loses its fibrous structure.

Experimental Procedure

For the hydrolysis of cellulose we used two solutions: (1) 10-percent lactic acid and (2) a mixture of 10-percent acetic acid and 10-percent sodium chloride.

In the preliminary experiments, approximately 1 g. of the sample was steeped in 100 ml. of the hydrolyzing reagent in an Erlenmeyer flask connected to a reflux condenser, and immersed in a boiling water bath for varying lengths of time. In later

experiments, the temperature was more accurately controlled and two sets of experiments were conducted as above at 87°C and 97°C. Commercial surgical cotton and viscose rayon were used as typical cellulosic materials. After treatment with the acid solutions, the samples were filtered on a Buchner funnel, washed free from acid, and dried at 50°C. The rate of hydrolysis was followed by measuring the D.P.'s of the various hydrolyzed celluloses in cuprammonium hydroxide solution. The cuprammonium hydroxide solution was prepared in accordance with the general procedure described originally by Clibbens and Geake [2], but with modifications and improvements proposed by O. A. Battista [1]. A 3-liter Erlenmeyer flask was filled with a mixture of 2.6 liters of concentrated ammonia (density = 0.88) and 0.4 liter of distilled water. One hundred and eighty grams of fine copper gauze, either cut into pieces or rolled up into a cylinder, was steeped in the mixture. The mouth of the flask (see Figure 1) was closed by a rubber stopper carrying a J-shaped fritted glass tube, *A*, of *C* porosity, a glass tube, *B*, bent at a right angle, and another glass tube, *C*, bent at an acute angle, with its end drawn out into a capillary. *B* and *C* were about 2 inches above the level of the solution, while *A* reached almost to the bottom of the flask. The flask was completely wrapped in black glazed paper and immersed in a bath of ice and salt. It is very important to keep the solvent very cold throughout its preparation. If its temperature is allowed to rise above 10°C. there is danger that excessive amounts of nitrous acid will form. Air, led through a wash bottle containing concentrated ammonia, was then passed through the fritted glass tube *A*, with tube *C* open and *B* closed. The concentrated ammonia in the washing bottle was replaced at least twice during an 8–12-hour period of generation in order to avoid depleting the ammonia concentration of the solvent and thus to attain a satisfactory final ammonia concentration. After about 12 hours, the current of air was stopped, *C* was closed, *A* was disconnected from the ammonia wash-bottle, and a portion of the solution was taken out through *A* by passing compressed nitrogen, led through a wash-bottle containing alkaline pyrogallol to remove any oxygen, through *B*. This solution was compared colorimetrically with a standard solution containing 15 g. Cu/liter (that is, 59 g. $CuSO_4 \cdot 5H_2O$/liter). When the solution became slightly more concentrated than the standard, the air supply was stopped and the solution was transferred by means of compressed, oxygen-free nitrogen to another 3-liter Erlenmeyer flask which was completely wrapped in black paper. The flask was closed tightly by means of a rubber stopper carrying a glass tube bent at a right angle, the longer end leading to the bottom of the flask, and two other glass tubes, similar to *B* and *C* above, whose ends went in about 2 inches below the stopper. After all the solution was transferred, 3 g./liter of sucrose was added to it, and oxygen-free nitrogen was passed through it for about 15 minutes, tube *B* being closed and *C* open.

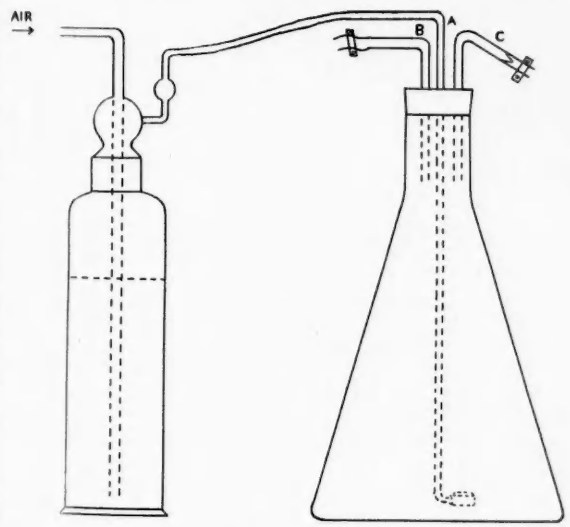


FIG. 1.

The solution was analyzed for Cu and NH_3 as indicated below, and the final solution was brought up to 15 ± 0.1 g. Cu/liter and 200 ± 10 g. NH_3/liter by adding a mixture of concentrated ammonia and distilled water in the required proportions. The diluting solution was transferred from a flask by means of compressed nitrogen. After the solution was brought up to the right concentrations, oxygen-free nitrogen was passed through it for about 15 minutes; then all the outlet tubes were tightly clamped and the flask was stored in a refrigerator.

Analysis for NH_3. Two ml. of solution was pipetted out and added slowly to 50 ml. of standard approximately 1*N* sulfuric acid in a 250-ml. Erlenmeyer flask, cooled in ice, with the tip of the pipette touching the bottom of the flask. Excess of acid was back-titrated against standard approximately 1*N* sodium hydroxide, using methyl red as indicator.

Analysis for Cu [8]. Ten ml. of solution was diluted with about 25 ml. of distilled water and the

ammonia was evaporated by boiling. The copper, which was precipitated, was first dissolved in concentrated sulfuric acid, 2 drops of liquid bromine was added, and the solution was boiled until all excess bromine was removed. The solution was then neutralized with concentrated ammonia and the excess ammonia was neutralized with glacial acetic acid, care being taken that not more than 5 to 6 drops of acetic acid was in excess. Solid potassium iodide was then added and the liberated iodine was titrated against standard 0.1*N* sodium thiosulfate, using starch as indicator toward the end-point. The copper content might preferably be determined by means of a calibrated photoelectric colorimeter. This method is rapid and equally accurate.

Three liters of solution were made up at a time. For daily use, part of the solution was transferred to a small (500-ml.) flask. Tubes slightly different from those used by Clibbens and Geake were employed for dissolving the cellulose. The dimensions of the tube are shown in Figure 2.

Cuprammonium solutions of cellulose of four to six different concentrations were usually made up, the concentrations ranging from about 0.2 to 1 percent. The dissolving tube was half filled with the solution, which was transferred from the flask by means of compressed oxygen-free nitrogen. Some of this solution was allowed to flow out through the capillary, *A*, the clip was tightened, and any air trapped in the rubber tubing was removed by pressing. The sample, weighed in black glazed paper and rolled up into a "cigarette," was then transferred to the tube, and the tube was completely filled with the solution. The glass stopper, *B*, was next inserted so that some of the solution overflowed through the capillary. The stopper was then closed and fastened by copper wire. Small spirals of thick copper wire were used as stirrers to keep the contents of the tubes well stirred during solution. The tube was wrapped in black glazed paper and left overnight on a radius of a wheel rotated at 6 r.p.m.

Viscosities were measured at 25° ±0.1°C in an Ostwald-Fenske type of viscometer. The dissolving tubes themselves were not used for viscosity measurements since the kinetic-energy corrections involved were too large. It has been experimentally checked that the flow time changes only negligibly in the period of 10–15 minutes, during which the solution is exposed to the atmosphere after it is introduced into the viscometer. The viscosity of the solvent was checked occasionally, and was found to remain almost constant.

The results are expressed, as usual, in η_{rel}, η_{sp}, η_{sp}/c and $\ln \eta_r/c$. The D.P.'s were calculated by the modified Staudinger equation

$$\text{D.P.} = 260 \left[\frac{\eta_{sp}}{c} \right]_{c \to 0},$$

and by the Kraemer equation

$$\text{D.P.} = 260 \left[\frac{\ln \eta_r}{c} \right]_{c \to 0}.$$

When a large number of samples must be processed, Battista's basic D.P. method at 0.5-percent concentration may be used in preference. This method is rapid and gives the same D.P. values as the more elaborate methods described above. The values given by the Staudinger and Kraemer equations are fairly concordant over the lower D.P. ranges (D.P. < 400), but show divergences for higher D.P. values.

The results of the various experiments with surgical cotton and viscose rayon are given in Table I and Figures 3 to 11. Only $\left[\frac{\eta_{sp}}{c} \right]_{c \to 0}$ and the Staudinger D.P.'s are given here.

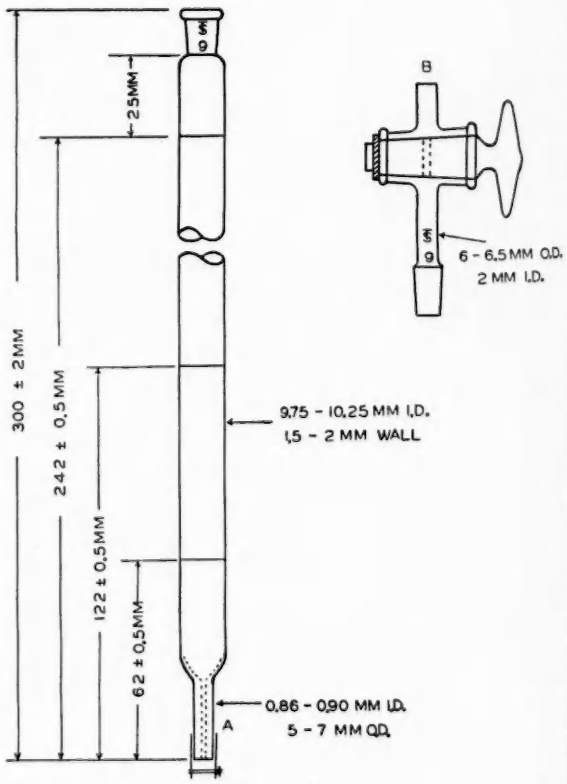


FIG. 2.

Discussion of Experimental Results

The results show a very interesting and unexpected behavior. In the case of surgical cotton (Figure 11) the hydrolysis curve consists of two distinct parts: an initial, very rapid rate of hydrolysis, from D.P. 2,500 to D.P. 400, followed by a slower rate of hydrolysis down to D.P. 250. After this, the curve levels out, and practically no more hydrolysis occurs. For comparison, the hydrolysis curve for random hydrolysis is also plotted. This has been calculated as follows:

Assuming a random hydrolysis of cellulose at a rate k, the D.P. at any time t can be shown to be:

$$\text{D.P.} = \frac{e^{kt/2} + e^{-kt/2}}{e^{kt/2} - e^{-kt/2}} = \coth \frac{kt}{2}. \quad * \qquad (1)$$

Since the initial D.P. of cellulose is 2,500 and not infinity, as equation (1) would give, this equation should be written

$$\text{D.P.} = \coth \frac{k(t + t')}{2},$$

where t' is found by putting D.P. = 2,500 at $t = 0$. The values of the function $\coth k(t + t')/2$ for different values of $k(t + t')$ can be obtained from the Smithsonian Tables for hyperbolic functions, kt' can be calculated by the above method, and hence kt can be found. The values are given in Table II and plotted in Figure 11.

This treatment is admittedly approximate, since the value of k is different in the middle (k_1) and end (k_2) of the molecule ($k_1 = 0.305 \times 10^{-4}$, $k_2 = 1.07 = 10^{-4}$). However, since the ratio $k_2/k_1 = 3.5$ is not very large, this assumption of one value for k should not change the general nature of the curve.

As can be seen distinctly, the experimental curve differs in two important respects from the theoretical curve for random hydrolysis. In the initial portion of the hydrolysis, the experimental curve is steeper than the theoretical, indicating a more rapid hydrolysis than that expected for a random hydrolysis of 1,4-glycosidic bonds. In the latter portion, whereas the theoretical curve continues to fall towards lower D.P. values, the experimental curve flattens out. Our experimental results are therefore in direct contrast to theoretical expectations. While random hydrolysis suggests the possibility of carrying the hydrolysis at a uniform rate down to glucose, our experiments show that under the conditions used by us there is an initial rapid hydrolysis at preferred spots, at a rate much more rapid than the rate of hydrolysis of 1,4-glycosidic bonds given by Stamm and Cohen [10] as 7.05×10^{-6} in 85-percent phosphoric acid. This rapid hydrolysis continues only up to the stage when a "limit hydrocellulose" is formed. Further action of acids has no appreciable effect on this "limit hydrocellulose," which for cotton has a D.P. of about 250.

If the theoretical curve is computed on the following assumptions: (*a*) the cellulose molecule has approximately 40 weak acid-sensitive bonds, one per 60 glucose anhydride units; (*b*) the acid attacks these weak bonds first, leaving the 1,4-β-glycosidic bonds intact; (*c*) there is a random hydrolysis of the weak acid-sensitive bonds—then it fits the experimental curve much more closely than that drawn on the assumption of a random hydrolysis of 1,4-β-glycosidic bonds. This indicates that the above assumptions regarding the structure of cellulose are more valid than the classical concept of the uniformity of all bonds in the cellulose molecule. The values of kt, and $\coth \frac{k(t + t')}{2}$ calculated as in Table II, are given in Table III and plotted in Figure 12.

Similar behavior has been observed by Davidson [3] in the action of dilute mineral acids on native cotton. He finds that the rates of change of the properties—for example, tensile strength, copper number, fluidity, percent loss of weight on alkali boiling—of the hydrocellulose so formed become negligible after a certain length of treatment, and that further action of acids has no effect. Unfortunately he has not followed the rate of hydrolysis by D.P. measurements, although he finds that the hydrocellulose in the limiting stage has a specific viscosity of 0.5 for a 0.5-percent concentration, which is about that found by us for our "limit hydrocellulose" by graphical interpolation. It thus seems to be definitely established that under mild conditions of hydrolysis, whether by mineral or by organic acids, hydrolysis of cotton cellulose comes to a standstill at a definite stage, when the material has a D.P. of about 250.

A slightly different behavior is shown by viscose rayon. Here the hydrolysis proceeds at a uniform rate until a D.P. of about 60 is reached, after which, once again, the hydrolysis comes to a standstill. In the results tabulated here, we have shown this be-

* Private communication from Prof. A. V. Tobolsky, Princeton University.

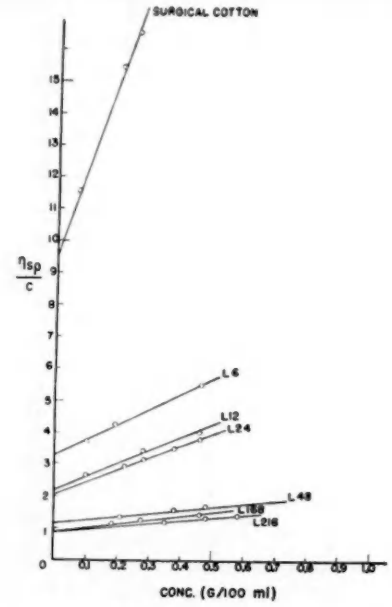


FIG. 3. *Surgical cotton hydrolyzed with 10-percent lactic acid at boiling water bath temperature.*

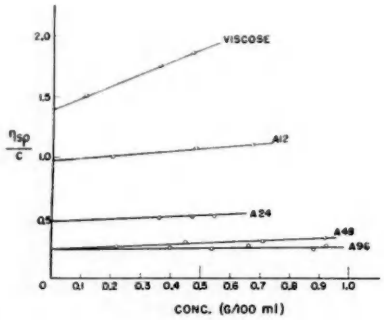


FIG. 4. *Viscose rayon hydrolyzed with 10-percent acetic acid and 10-percent NaCl at boiling water bath temperature.*

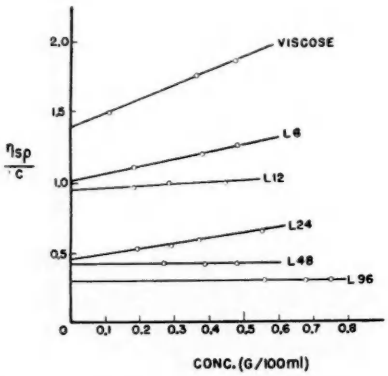


FIG. 5. *Viscose rayon hydrolyzed with 10-percent lactic acid at boiling water bath temperature.*

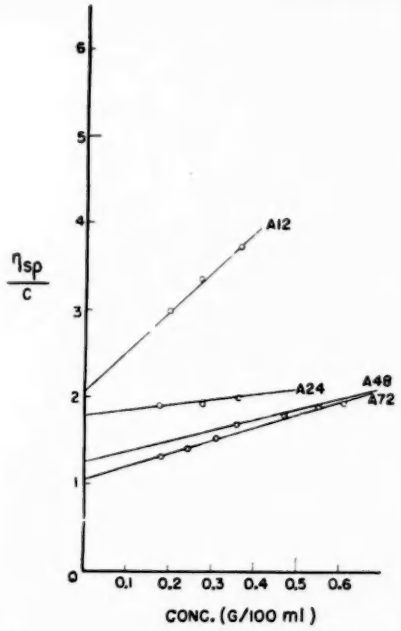


FIG. 6. *Surgical cotton hydrolyzed with 10-percent acetic acid and 10-percent NaCl at 87°C.*

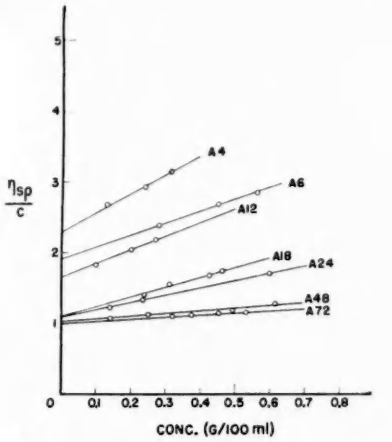


FIG. 7. *Surgical cotton hydrolyzed with 10-percent acetic acid and 10-percent NaCl at 97°C.*

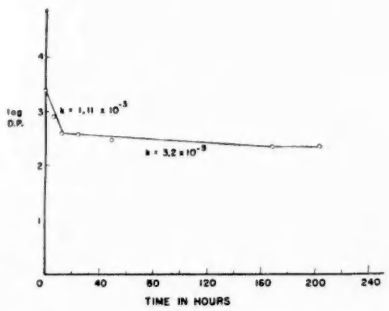


FIG. 8. *Surgical cotton hydrolyzed with 10-percent lactic acid at boiling water bath temperature.*

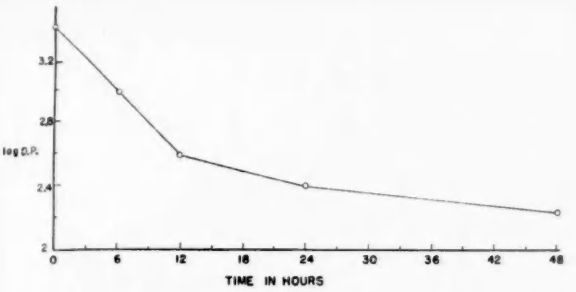


FIG. 9. *Surgical cotton hydrolyzed with 10-percent acetic acid and 10-percent NaCl at boiling water bath temperature.*

havior with organic acids. In further experiments with 1*N* hydrochloric acid at 60°C, we have found the same behavior, the viscose reaching a D.P. of 62 in 12 hours' treatment, after which a further 12 hours' treatment has given a D.P. of 52.

As stated earlier, these experiments should provide a crucial test for the new theory of cellulose

TABLE I. DEGREES OF POLYMERIZATION OF SURGICAL COTTON AND VISCOSE RAYON, HYDROLYZED WITH (1) 10-PERCENT ACETIC ACID AND 10-PERCENT SODIUM CHLORIDE; (2) 10-PERCENT LACTIC ACID FOR VARIOUS LENGTHS OF TIME

Sample	$[\eta]$	D.P.	Sample	$[\eta]$	D.P.
Surgical cotton	9.6	2,496	Surgical cotton		
L_6	3.3	858	87° A_{12}	2.09	543
L_{12}	2.2	572	87° A_{24}	1.8	468
L_{24}	2.05	533	87° A_{48}	1.25	325
L_{48}	1.15	299	87° A_{72}	1.05	273
L_{168}	0.9	234	97° A_4	2.29	595
L_{216}	0.9	234	97° A_6	1.92	499
Viscose rayon	1.4	364	97° A_{12}	1.68	437
			97° A_{18}	1.1	286
A_{12}	0.9	234	97° A_{24}	1.1	286
A_{24}	0.475	124	97° A_{48}	1.02	265
A_{48}	0.234	60	97° A_{72}	1.0	260
A_{96}	0.25	65			
L_6	1.02	265			
L_{12}	0.95	247			
L_{24}	0.45	117			
L_{48}	0.39	101			
L_{96}	0.3	78			

NOTE: L_6, L_{12} ··· denote hydrolysis with 10-percent lactic acid for 6, 12 ··· hours at boiling water bath temperature.

A_6, A_{12} ··· denote hydrolysis with 10-percent acetic acid and 10-percent sodium chloride for 6, 12 ··· hours at boiling water bath temperature.

87° A_{12} ··· denote hydrolysis with 10-percent acetic acid and 10-percent sodium chloride at 87°C for 12 hours . . .

97° A_4 ··· denote hydrolysis with 10-percent acetic acid and 10-percent sodium chloride at 97°C for 4 hours . . .

$[\eta]$ denotes $\left[\frac{\eta_{sp}}{c}\right]_{c\to 0}$.

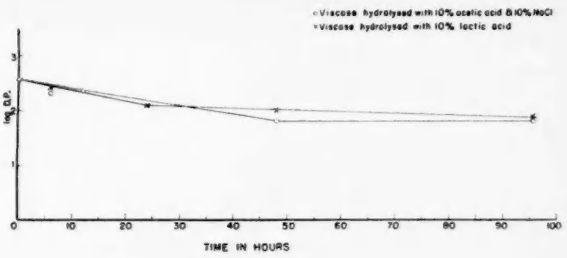


FIG. 10.

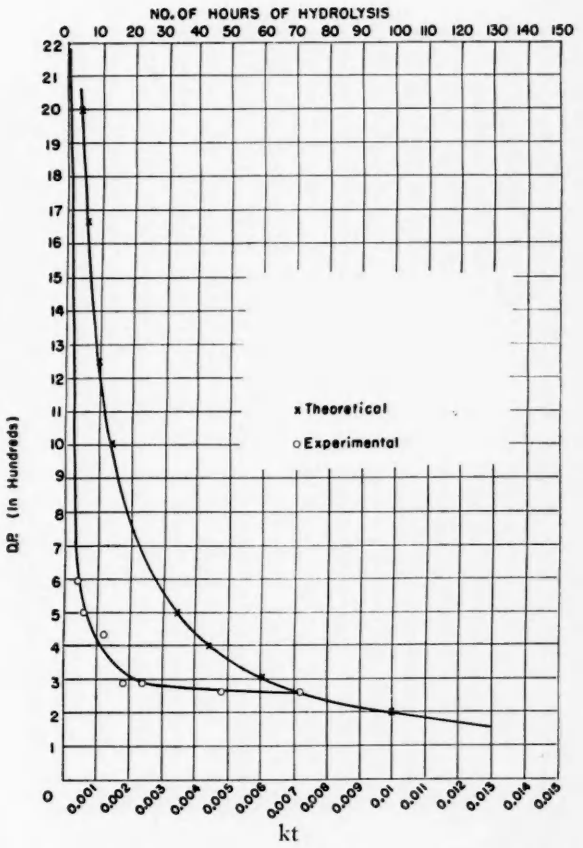


FIG. 11. *Comparison of theoretical curve for random hydrolysis and experimental curve.*

TABLE II

$\frac{k(t+t')}{2}$	$k(t+t')$	kt	D.P. $= \coth\frac{k(t+t')}{2}$
0.0004	0.0008	0.00	2500.00
0.0005	0.0010	0.0002	2000.00
0.0006	0.0012	0.0004	1666.67
0.0008	0.0016	0.0008	1250.00
0.001	0.002	0.0012	1000.00
0.002	0.004	0.0032	500.00
0.0025	0.005	0.0042	400.00
0.0033	0.0066	0.0058	303.03
0.005	0.01	0.0092	200.00

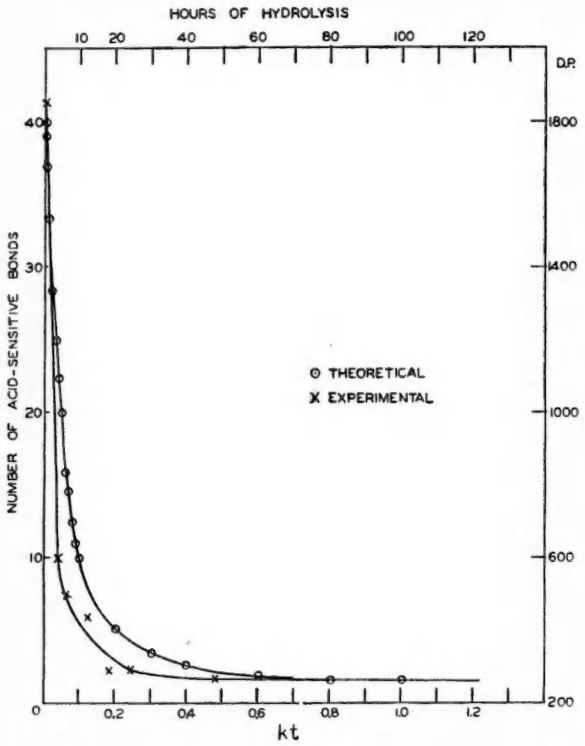


FIG. 12. *Comparison of theoretical curve for random hydrolysis of acid-sensitive bonds and experimental curve.*

structure. The results clearly indicate that the classical formula for the cellulose molecule is quite inadequate to explain this behavior of cellulose on mild hydrolysis. The hypothesis that the reagent attacks only the amorphous region of the cellulose molecule and that the reaction stops after the 1,4-glycosidic bonds in the amorphous region have been hydrolyzed meets with several difficulties. In the first place, the ratio of amorphous and crystalline areas calculated from these results is very much different from that calculated by physical methods [6]. In the second place, moisture absorption should decrease steadily as the increasing length of acid treatment progressively removes the amorphous material. Davidson, however, in his work referred to previously, has found that the "relative moisture absorption" does not obey this requirement and in one case it actually passes through a minimum and then increases as the hydrolysis continues. In the third place, in homogeneous solution, such as in 85-percent phosphoric acid, where similar degradation results were obtained, the "crystalline regions in the cellulose are broken up and the acid acquires access to every linkage," according to Davidson.

On the basis of the new concept, the results can be explained in a very simple way. If the cellulose molecule consisted of units of building bricks connected together by hemiacetal or acetal bonds, these, being very sensitive to acids, would be first attacked by any acid treatment. Once these sensitive bonds are removed and the "limit hydrocellulose" stage has been reached, further action of acids, if mild, has no appreciable effect on the 1,4-glycosidic bonds. This theory thus explains clearly why there is such a rapid initial hydrolysis at a rate much greater than the rate of hydrolysis of 1,4-glycosidic bonds in mineral acids. It also explains why the hydrolysis comes to a standstill after a certain stage is reached. The limit hydrocellulose has a D.P. $\sim$ 250 in the case of native cotton, and D.P. $\sim$ 60 for viscose.

From later experiments carried out under accurately controlled temperature conditions we have calculated the various velocity constants, the energy of activation from the integrated form of Arrhenius' equation, and the entropy of activation, using Eyring's equation for absolute reaction rates. The following values have been found:

For surgical cotton hydrolyzed with 10-percent acetic acid and 10-percent sodium chloride,

$$K_{97} = 3.43 \times 10^{-3},$$
$$K_{87} = 1.27 \times 10^{-3},$$

for the initial reaction of hydrolysis from the original D.P. 2,500 to about D.P. 550–600. Using Arrhenius'

TABLE III

$\frac{k(t+t')}{2}$	$k(t+t')$	kt	D.P. $= \coth \frac{k(t+t')}{2}$
0.025	0.050	0	40.008
0.0256	0.0512	0.0012	39.071
0.0270	0.0540	0.0040	37.046
0.0350	0.070	0.020	28.583
0.040	0.080	0.030	25.013
0.0450	0.090	0.040	22.237
0.050	0.10	0.05	20.017
0.060	0.120	0.070	16.687
0.070	0.140	0.090	14.309
0.080	0.160	0.110	12.527
0.090	0.180	0.130	11.141
0.1000	0.2000	0.150	10.033
0.200	0.400	0.350	5.0665
0.300	0.600	0.550	3.4327
0.400	0.800	0.750	2.6319
0.600	1.200	1.150	1.8620
0.800	1.600	1.550	1.5059
1.000	2.000	1.950	1.3130

equation,

$$E = R\frac{T_1T_2}{\Delta T}\ln\frac{k_2}{k_1}$$
$$= 26{,}300 \text{ calories.}$$

From Eyring's equation for absolute reaction rates,

$$K = \frac{k_0 t}{h}e^{-\Delta H^{\ddagger}/RT}e^{\Delta S^{\ddagger}/R},$$

the entropy of activation, $\Delta S^{\ddagger} = -11.4$ e.u.

Similar calculations, when carried out on the random hydrolysis of cellulose, starch, methyl glycosides, maltose, cellobiose, etc., from the available data, all show a positive value for the entropy change in the reaction. This difference in the sign of the entropy change may have some significance in the interpretation of the actual mechanism of the heterogeneous acid degradation as against homogeneous degradation.

Summary

Experiments have been carried out on the heterogeneous hydrolysis of surgical cotton and viscose rayon, using (1) a mixture of 10-percent acetic acid and 10-percent sodium chloride, (2) 10-percent lactic acid, at the temperature of the boiling water bath, 87°C and 97°C, and of viscose rayon using (3) 1*N* hydrochloric acid at 60°C. The hydrolysis is very rapid in the initial stages, and comes to a standstill when the D.P. has reached about 250 for cotton and about 60 for viscose rayon. Further action of acids has no appreciable effect on the D.P.

These results are regarded as a partial confirmation of the new theory of cellulose structure—viz., that cellulose consists of "building bricks" or units of β-*D*-glucopyranose residues connected by 1,4-glycosidic bonds, these units being interconnected by hemiacetal bonds. Mild hydrolysis, under the conditions used by us, affects only the hemiacetal bonds, so that it stops after the "limit hydrocellulose" is formed. This has a D.P. ∽ 250 in the case of cotton and a D.P. ∽ 60 for viscose rayon.

The velocity constants and energy and entropy of activation for the initial hydrolysis from D.P. 2,500 to about 550–600 have been calculated for surgical cotton to be

$$K_{97} = 3.43 \times 10^{-3}, \quad K_{87} = 1.27 \times 10^{-3},$$
$$E = 26{,}300 \text{ calories},$$
$$\Delta S^{\ddagger} = -11.4 \text{ e.u.}$$

The negative entropy value may have some significance, since the entropy values calculated for a random hydrolysis in homogeneous systems on cellulose, starch, methyl glycosides, etc., are positive.

Acknowledgment

The authors would like to thank Dr. J. H. Dillon, Director of Research, the Textile Research Institute, for his continued interest in the work, for his many valuable suggestions, and for reading the manuscript of this paper; and Miss Corneil Messler, for making the drawings.

Literature Cited

1. Battista, *Ind. Eng. Chem., Anal. Ed.* **16**, 351 (1944).
2. Clibbens and Geake, *J. Text. Inst.* **19**, T77 (1928).
3. Davidson, *Shirley Inst. Mem.* **18**, 219 (1941); *J. Text. Inst.* **34**, T87 (1943).
4. Freudenberg, Kuhn, *et al.*, *Ber.* **63**, 1512 (1930).
5. Hiller and Pacsu, TEXTILE RESEARCH JOURNAL **16**, 564 (1946).
6. Magne *et al.*, *J. Am. Chem. Soc.* **69**, 1896 (1947).
7. Pacsu, TEXTILE RESEARCH JOURNAL **17**, 405 (1947).
8. "Scott's Standard Methods of Chemical Analysis," 5th Ed., New York, D. Van Nostrand Co., Inc., 1939, vol. 1, p. 368.
9. Sherrard and Froehlke, *J. Am. Chem. Soc.* **45**, 1729 (1923).
10. Stamm and Cohen, *J. Phys. Chem.* **42**, 921 (1938).
11. Willstätter and Zechmeister, *Ber.* **46**, 2410 (1913).
12. Wolfrom and coworkers, *J. Am. Chem. Soc.* **59**, 282 (1937); *ibid.* **60**, 1026 (1938).

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Imparting Water-Repellency to Textiles by Chemical Methods: A Review of the Literature*

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Abstract

The literature relating to the water-repellency of textile materials has been surveyed for those articles and patents dealing with the production of this property by chemical methods. The 332 pertinent references found have been abstracted and classified on the basis of the type of compound used to impart water-repellency. No attempt has been made at critical evaluation. Reactions, where known, have been described with the aid of equations. Additional references for collateral reading are given. An index which has been compiled of the chemical water-repellent agents proposed is being published by the U. S. Department of Agriculture as Research Publication AIC—179.

Introduction

The production of water-repellent textiles has become a matter of increasing importance in recent years and several hundred patents have been granted, covering various methods of producing water-repellency. The present work offers, without pretense of evaluation, a review of the references gathered from the patent literature on the production of water-repellency by chemical methods, as well as from several selected journal articles, which, it is hoped, may prove useful to workers in this field. The references were collected through October, 1947, and an attempt was made to consult all references as originals or photostats. Where this was impossible, secondary sources were employed and these are indicated in Literature Cited. An effort has been made to make the review as complete as possible, but it is probable that some references have been overlooked. Approximately 200 references were rejected as not falling into the class of chemical water-repellents.

By "chemical water-repellency" is meant repellency obtained by processes which involve (or are believed capable of involving) a chemical reaction of the water-repellent agent with the textile fabric or with itself to give a fabric more or less repellent to water but permeable to air.

Those methods of producing water-repellency by mechanical coating, by treatment with waxes, rubber emulsions, etc., have not therefore been included. Textiles so coated are referred to as being "waterproof" and generally have a continuous surface with very low air permeability. Water-repellency obtained by methods involving the production of metallic soaps is also excluded, although the formation of polymers produced *in situ* is described.

Among the references examined, the following are suggested for collateral reading, as giving specific discussions of various phases of water-repellency [50, 55, 173, 238, 254, 319].‡

The scope of the present review does not permit a lengthy discussion of the theory of water-repellency, but it should be pointed out here that many factors affect the water-repellency of a fabric. The chief physical factor is the construction of the fabric, and Baxter and Cassie [22] have studied construction extensively. They go so far as to state that the familiar "ideal" example of water-repellency—that obtained by a feather from a

* The Introduction and Parts I and II of this review appear in this issue. The rest, Parts III–X, will appear in the August issue.

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‡ The references for the complete review have been arranged in alphabetical order and numbered consecutively from 1 to 332. Those referred to in each section appear at the end of the section under "Literature Cited," and the original numbers have been retained.

duck's back—owes its effectiveness less to the presence of a water-repellent agent than to the theoretically excellent arrangement of small barbules on the feather barbs which are rigidly fixed to resist distortion by the surface tension of water drops in such manner as to allow the drops to form into spheres and roll off in the traditional manner. These workers conclude that more attention should be given to the construction of fabrics, a conclusion supported by the results obtained by the U. S. Army Quartermaster Corps, in work recently completed [273]. An excellent review and analysis of the theory of water-repellency of textile fabrics, containing 85 references, has lately been published by Rowen and Gagliardi [254].

In a review of chemical methods of obtaining water-repellency it is pertinent to point out some of the factors concerned when the physical factors, such as fabric construction, are identical.

Most of the natural fibers, after purification, are hydrophilic and must be made hydrophobic by various treatments, the variety and number of which are attested to by the articles and patents discussed in this paper. It is not entirely appreciated, perhaps, that water-repellency is not attained merely by coating a fiber with paraffin or similar material in the small amounts which are necessary for the process to be commercially practical and for the fabric to retain the porosity needed for transpiration. In some cases, indeed, this type of treatment is quite successful, as with the widely used metallic soaps. Neither is it appreciated perhaps that long-chain hydrocarbons such as the octadecyl groups generally used are in some cases unnecessary. For example, organo-silicon polymers are sufficient to give excellent, although not necessarily permanent, water-repellency, as is shown by the application of mono- or dimethylchlorosilane to cloth. On the other hand, cellulose acetate fabric, which from structural considerations would be expected to be considerably more hydrophobic than cotton, shows no significant water-repellency.

Kursanov and Selkina [187] have studied various quaternary compounds with the object of determining the optimum constitution to give water-repellency. They found that alkyl groups 8 to 14 carbon atoms long gave little water-repellency, whereas chains with 16 to 18 carbon atoms gave good results. Zerner and Pollak [332] have stated that sometimes slight differences in chemical structure have a considerable influence on water-repellency. They also worked with quaternary compounds and cite some examples of the preparation of materials where the water-repellencies obtained are good when the number of carbon atoms connecting two amide radicals is odd, but are poor when the chain is even. From the rather meager evidence given they infer that repellency is favored when the reactive polar groups are oriented in the same direction; *i.e.*, when the number of methylene groups is odd. The theory of the action of chemical water-repellent agents is apparently very poorly developed; hence it must suffice to point out that the factors concerned are not so simple as they may appear at first inspection.

A review of methods of testing the water-repellency of fabrics has been published lately [254] and descriptions of some of the various methods may be found in the following references [60, 187, 273, 274, 307, 319].

No criticism of the methods reviewed has been attempted. It is obvious, for instance, that some of the patent claims are exaggerated or impossible.

Subdivision of the references has been based on the nature of the functional group of the water-repellent agent—that is, the reacting group. Thus an ester halide of a dicarboxylic acid which reacts with cellulose to eliminate hydrogen chloride and form a cellulose ester is classified with esterifying agents in group I. A diester of a dicarboxylic acid which reacts with cellulose by transesterification to produce a product identical with that in the case described above is classified in group III (esters *). A compound in which silicon might be connected to a quaternary nitrogen is classified in group II (quaternary nitrogen compounds) but is cross-referenced in group X (silicon compounds). The selected groups are as follows:

I. Acid Halides, Anhydrides, and Other Esterifying Agents
II. Quaternary Nitrogen Compounds
III. Esters and Urethanes
IV. Amines, Amides, and Related Compounds
V. Aldehydes
VI. Polymers Formed *in situ*
VII. Ethers, Epoxides, and Related Compounds
VIII. Cyanates, Thiocyanates, and Related Compounds
IX. Urea Derivatives
X. Silicon Derivatives and Miscellaneous Compounds

* Parts III–X will appear in the August issue.

In each group the chemical reactions have been summarized, including the preparation of the compound where considered necessary, and the chemistry of the reactant with itself or with the cloth where this has been established. Interpretations have occasionally been offered. Equations have been shortened where possible by the elimination of unimportant by-products and the abbreviation "HO-Cell" has been used to represent cellulose with reactive hydroxyl groups. Wherever possible, one or more typical reactions have been discussed in some detail and all references in that classification have been included if only by reference number.

During the compilation of the references a list of several thousand compounds used in the manufacture of water-repellent agents was assembled. With the object of enabling the worker to locate quickly any patents or reference in the literature relating to a given type of compound, an index has been prepared which consists of the principal types of organic compounds concerned, with the appropriate reference number. For example, an alkyl amide quaternary compound which is also an ether is listed under "Ethers" and "Alkyl Amides," as well as under the particular quaternary heading. This index is not part of this paper but has been published by the U. S. Department of Agriculture as Research Publication AIC—179. The references in the index have the same numbers as the items listed in the "Literature Cited" sections in this review.

Literature Cited

(Introduction)

22. Baxter and Cassie, *J. Text. Inst.* **36**, T67–90 (1945).
50. Burnand, *Teintex* **4**, 27–33, 97–104, 155–63 (1939).
55. Chwala, *Melliand Textilber.* **19**, 905–10 (1938).
60. Croen, *Cotton* (Atlanta) **107**, 63–6 (1943).
173. Jackson, *Textile Recorder* **62**, 60–1 (1945).
182. Karrer, Ger.P. 438,324 (1926).*
187. Kursanov and Selkina, *J. Applied Chem.* (U.S.S.R.) **16**, 36–46 (1943).
238. Pascalis, *Tiba* **17**, 337–45 (1939).
254. Rowen and Gagliardi, Research Paper RP1762, *J. Research Natl. Bur. Standards* **38**, 103–17 (1947); *Am. Dyestuff Reptr.* **36**, 533–40 (1947).
273. Slowinske and Pope, *Am. Dyestuff Reptr.* **36**, 108–21 (1947).
274. Smith and Wellington, *Rayon Text. Mo.* **28**, 332–4, 371–3, 423–6 (1947).
307. Wakeham and Skau, *J. Am. Chem. Soc.* **67**, 268–72 (1945).
319. Wengraf and Schwarz, *Am. Dyestuff Reptr.* **31**, 551–8 (1942).
332. Zerner and Pollak, TEXTILE RESEARCH **14**, 242–5 (1944).

* Throughout the "Literature Cited" lists in this review the following abbreviations have been used in the references to patents: U.S.P.—U. S. Patent; B.P.—British Patent; Fr.P.—French Patent; Ger.P.—German Patent; etc.

Part I. Acids, Acid Halides, Acid Anhydrides, and Other Esterifying Agents

The production of water-repellent textiles by the reaction of organic acid derivatives with the cloth has been studied to a considerable extent. This type of treatment involves the reaction of a long-chain acid anhydride, halide, or other acid derivative with the hydroxyl groups of cellulose or with the amino groups of animal or animalized fiber.

The esterification of cotton cloth is of interest, since the product probably would be fairly stable to laundering and fast to dry-cleaning. However, even the partial acetylation of cotton is attended with considerable difficulty and the long-chain acid derivatives require much more drastic conditions of treatment than the short-chain acids.

The esterification of cellulose with *higher fatty acid derivatives* has been studied in detail by a number of workers [111, 114, 185, 243]. It has been claimed that cellulose cannot be esterified to a high degree by long-chain fatty acid anhydrides [237], but it should be noted that water-repellency might very well be obtained with only a slight amount of esterification. It does not therefore seem unreasonable that sufficient esterification may take place to impart water-repellency [111, 114, 185, 243]. While the work on complete esterification of cellulose is of value, the results may be misleading when translated into partial esterification of cloth. The complete and incomplete reactions are identical in principle, but vary greatly in detail.

Moeller [201, 202, 203, 204, 205, 206, 208, 209, 210, 216] claims that cellulosic material exposed to the vapors of *thionyl chloride* for a short period of time is rendered water-repellent.

Karrer [184] holds one of the earliest patents dealing with water-repellency of cloth induced by the treatment with *high-molecular-weight acid halides*. Cellulose in the form of cloth or yarn is treated with 12–20% caustic for 2 hours, squeezed dry, and soaked in an organic solution of stearic or palmitic acid chloride for 1 to 2 hours. The finished product is said to have a soft feel and to be water-repellent.

By far the largest number of patents in this class are claimed by Nathansohn [119, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230]. His work includes the use of stearic, palmitic, lauric, and other *long-chain anhydrides*, as well as the corresponding acid halides, the reactions being carried out in neutral or alkaline organic media. The methods of application include spraying, dipping in organic solvent solutions or aqueous emulsions, and impregnation with the fused anhydride. In all cases an after-treatment is included, which generally consists of a baking at temperatures ranging from 70° to 100°C for times up to 24 hours.

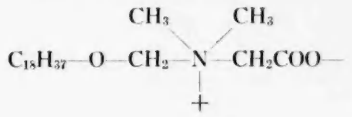
The Studiengesellschaft für Faserveredelung m.b.H., to which Nathansohn assigned one of the previously mentioned patents [229], has also claimed the use of *high aliphatic acid anhydrides* [72, 96] and their emulsions [298].

The I. G. Farbenindustrie A.G. [129] has also claimed the use of emulsions of high-molecular acid anhydrides for producing water-repellency.

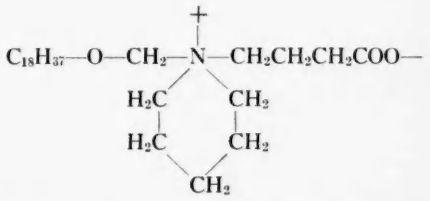
The Deutsche Kunstseiden-Studiengesellschaft m.b.H. has patented the use of *high-molecular acid chlorides* [70], such as palmityl chloride, and anhydrides [71], such as stearyl anhydride, as water-repellents, and the Fabrique de Produits Chimiques (formerly Sandoz) in Switzerland has been granted a patent [54] which covers the use of emulsions of high-molecular acid anhydrides and chlorides.

It is claimed by the Deutsche Hydrierwerke A.G. that the use of high-molecular acid anhydrides alone is not necessary [68]. They have patented the use of a *mixture of high-molecular acids and low-molecular acid anhydrides* which, they claim, will impart water-repellency which is not reduced by dry-cleaning or washing with soap. As an example they cite a mixture of 1% each of technical montanic acid and chloracetic anhydride in benzene. Cloth is soaked in this solution for 15 minutes, shaken out, dried, and finally heated at 110°–120°C for an hour.

Orthner *et al.* hold a patent [163, 235, 236] covering the use of a *betaine-type* compound which they claim will impart water-repellency to textiles which have been treated in a 1% solution, dried, and heated to about 140°C for approximately ½ hour. Examples of the compounds covered are:



Octadecoxymethyl betaine



N-octadecoxymethyl-*N*-amylene-γ-butyric acid

The I. G. Farbenindustrie A.G. has patented [161] the use of aliphatic *acid chlorides, anhydrides, or isocyanates* containing from 4 to 10 carbon atoms with pyridine, quinoline, dimethylaniline, or other tertiary amines.

Lant [186, 188, 189, 190, 191] has patented the use of high-molecular acid chlorides with tertiary amines, particularly pyridine, as a water-repellent.

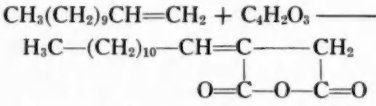
Singer [271] claims that textile materials and paper may be made water-repellent by a treatment with *naphthenic anhydride or chloride* with or without a tertiary base such as pyridine. The textile is soaked in a solution of the acid derivative, dried, and heated. The excess reagent is removed by extraction with a suitable solvent.

Similar claims are made by the I. G. Farbenindustrie A.G. in a patent [124,160] which claims the use of naphthenic anhydride, chloride, or isocyanate as well as similar derivatives of benzoic and substituted benzoic acids. Tertiary bases such as pyridine, quinoline, etc. may be used.

Moncrief and Bates [217] have described a process for the treatment of cotton or rayon yarn and cloth with an esterification medium consisting of the *anhydride of a polycarboxylic acid* and a long-chain acid. Two of the combinations used were adipic anhydride and stearic acid, and citric anhydride and lauric acid. Cellulosic fabrics were heated with the mixture in a nonsolvent liquid for several hours at 100°–150°C.

The I. G. Farbenindustrie A.G. [118, 128, 130, 145] has described the use of *inner anhydrides of dibasic carboxylic acids* containing saturated or unsaturated side chains. Products of this nature can be produced by the condensation, for example, of dodecylene with maleic anhydride:

$$CH_3(CH_2)_9CH{=}CH_2 + C_4H_2O_3 \longrightarrow$$



Dodecylidene succinic anhydride

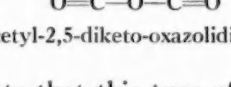
Cloth is dipped into a solution of the compound, squeezed to remove the excess, and dried in an oven at 100°C.

The I. G. Farbenindustrie A.G. [140] has patented the reaction between *β-hydroxy ethyl cellulose with acid chlorides or anhydrides* of high molecular weight to yield water-repellent materials.

Baldwin and Rogers [13] have described a process involving a treatment of cotton cloth with inner anhydrides of α-carboxyamino-carboxylic acids which are known as *2:5 diketo oxazolidines*. These may be produced as follows:

$$C_{16}H_{33}{-}CH(NH_2)COOH + ClCOOCH_3 \longrightarrow$$

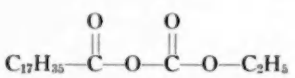
$$C_{16}H_{33}{-}CH(NHCOOCH_3)COOH \xrightarrow{SOCl_2}$$



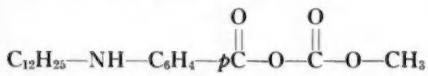
4-cetyl-2,5-diketo-oxazolidine

The authors state that this type of compound decomposes at about 130°C to give carbon dioxide and a putty-like material which renders the cloth water-repellent. While it is by no means certain that the reaction described by the authors takes place with the cloth, it is evident that such a reaction is possible by virtue of the anhydride linkage. However, a condensation probably occurs, with the deposition of a polyamide.

Kaase and Waltmann [106, 175] have used a large number of *mixed ester anhydrides* of which the following are examples:

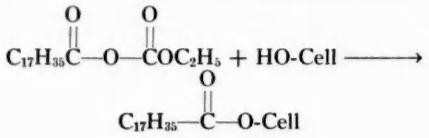


Ethyl stearyl carbonate



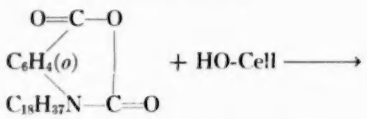
Methyl (*p*-dodecylamino benzoic) carbonate

These workers have impregnated cotton, linen, or woolen cloth either in organic solution or aqueous emulsion with the above type of compound. The textile was then heated for 2 minutes to 2 hours to volatilize the carbonic ester part of the molecule, resulting in the following probable reaction:



Cellulose stearate

Guenther and Haussmann [115, 166] have used certain derivatives of *isotoic anhydride* to produce water-repellent textile materials. They claim that cotton or rayon cloth can be made to react with compounds like *N*-octadecyl isotoic anhydride according to the following equation:



N-octadecyl isotoic anhydride

$$C_{18}H_{37}NH{-}(o)C_6H_4{-}COO\text{-Cell}$$

According to these workers, the cloth is treated for 5 minutes with a solution in organic solvent and dried for 1 hour at 110°C.

The I. G. Farbenindustrie A.G. has patented the treatment of textiles with *alkyl chlorocarbonates* to impart water-repellency [134, 141, 306]. Compounds such as octadecyl chlorocarbonate, cetyl chlorocarbonate, etc. are mixed with pyridine. The mixture is applied to the textile, which is heated to 90°C for 1 hour.

The Färberei A.G. [104] has patented the use of the same type of compound with the specification that the molecule contain more than 9 carbon atoms. The material is heated for only 2 minutes at 110°–120°C.

Waltmann and Wolf [316] have patented the use of substituted *carbamic acid chlorides* such as *N*-stearyl-*N*-butyl-carbamic acid chloride and *N*-palmityl-*N*-methyl carbamic acid chloride. The usual treatment is used, with baking from 10 minutes to 1 hour at 60° to 120°C.

Aelony [1] has patented the treatment of textiles with such compounds as *N-alkylmonophthalamide* following the usual impregnation, wringing, drying, and baking at 125°–150°C.

Engelmann and Pikl [81, 82] have patented the preparation and use of *phosphonium compounds* for the purpose of producing water-repellent textiles. The details of the preparation follow.

$$C_6H_5—CO—NH—CH_2OH \xrightarrow{PCl_3} C_6H_5—CO—NH—CH_2OPCl_2 \longrightarrow$$

Dichloro phosphorus ester

$$C_6H_5—CO—NH—CH_2POCl_2 \xrightarrow{2\,H_2O}$$

Phosphone dichloride

$$C_6H_5—CO—NH—CH_2PO(OH)_2$$

Phosphonic acid

Other compounds described by the authors are:

$$C_{18}H_{35}O—CO—NH—CH_2—PO(OH)_2$$
$$C_{17}H_{35}—CO—N(—CH_2—PO(OH)_2)—CH_2—N(—CO—C_{17}H_{35})—CH_2—PO(OH)_2$$

N, N'-methylphosphonic acid of distearamidomethane

Cloth when treated with a 2% to 4% aqueous solution of the ammonium salt of the phosphonic acid derivative and dried at 150°C is said to acquire a permanent water-repellent finish. While the authors do not offer this explanation, presumably the reaction produces cellulose phosphate both with the acid chloride and with the ammonium salt, similar to that occurring in the flameproofing of cotton cloth [193, 301].

Lommel and Münzel [194] have also claimed the use of *phosphonium compounds* with the provision that one of the four radicals is connected to the P atom by means of a secondary or tertiary carbon atom.

Engelmann and Pikl [83] have also worked with compounds derived from the reaction of *methylolamides* with compounds containing hydroxyl groups. They have produced:

$$C_{18}H_{37}N(H)—C(=O)—N(H)—CH_2OH + HOCH_2COOH \longrightarrow C_{18}H_{37}N(H)—C(=O)—N(H)—CH_2OCH_2COOH$$

N-carbomethoxymethyl-*N'*-octadecyl urea

It should be pointed out also that in many cases the above methylol compound may be replaced by the corresponding chloride, to yield the same product. Among examples listed are:

$$C_{17}H_{35}CO—NH—CH_2OCH_2PO(OH)_2$$

Stearamidomethoxy methyl phosphonic acid

$$C_{17}H_{35}CO—NH—CH_2OCH(CH_3)COOH$$

α-stearamidomethoxy propionic acid

$$C_{18}H_{37}OOC—NH—CH_2OCH_2COOH$$

N-carbo-octadecoxy-aminomethoxy acetic acid

Treatment of cloth is carried out in the same manner as for the phosphonium compounds.

In spite of the popularity of esterification as a means of obtaining water-repellency, it is surprising that so little attention has been given to the use of *ketenes* to obtain esters.

The Deutsche Hydrierwerke A.G. [69] has patented a method for rendering water-repellent such materials as "textiles, paper, leather, fur and the like" by a treatment with high-molecular ketenes. The ketenes used must contain at least 6 carbon atoms in the molecule and the reaction appears to be:

$$C_4H_9CH=C=O + HO\text{-}Cell \longrightarrow$$

Butyl ketene

$$C_4H_9CH_2COOCell$$

The ketenes are dissolved in organic solvents so as to give solutions of 1% to 3%, the materials being then impregnated and heated to 110°–120°C. Some of the examples cited are: caprylketene, laurylketene, cetylketene, and ketenes derived from montanic, naphthenic, adipic, and sebacic acids. Similar compounds are claimed by Hentrich and Hueter [121].

Sauer [259, 262] has patented the preparation of dialkyl and acylalkyl ketenes, both of which are claimed to give water-repellency provided the molecular weight is high enough. In both types,

$$C_{18}H_{37}(C_{16}H_{33})C=C=O$$

Octadecyl hexadecyl ketene

$$C_{12}H_{25}CO(C_{10}H_{21})C=C=O$$

Dodecanoic decyl ketene

the products would appear to be esters, following the reaction already mentioned. Examples of the dialkyl type, which are called "dialkylethenones," are: diheptylethenone, ethyldodecylethenone, octadecylhexadecylethenone, etc. Examples of the

second class include dodecanoyldecylethenone, octanoylhexylethenone, and propanoylmethylethenone.

The use of ketenes to produce esterification would have the advantage of yielding no by-products since the reaction is one of addition. However, a striking disadvantage in esterification by means of ketenes to produce water-repellency lies in the necessity for anhydrous conditions, since ketenes will react with even atmospheric moisture to yield acids.

Cellulose esters similar to those discussed in this section are prepared by the *transesterification* of cellulose with organic esters [132, 136, 198, 253]. These are discussed in the section entitled "Esters."

Literature Cited

(Part I)

1. Aelony, U.S.P. 2,398,272 (1946).
13. Baldwin and Rogers, U.S.P. 2,327,162 (1943).
54. Chemische Fabrik vormals Sandoz, Fr.P. 850,327 (1939).
68. Deutsche Hydrierwerke A.G., B.P. 515,908 (1939).
69. Deutsche Hydrierwerke A.G., B.P. 522,204 (1940).
70. Deutsche Kunstseiden-Studiengesellschaft m.b.H., Berlin, Ger.P. 616,722 (1935).
71. Deutsche Kunstseiden-Studiengesellschaft m.b.H., Berlin, Ger.P. 619,228 (1935).
72. Deutsche Kunstseiden-Studiengesellschaft m.b.H., Berlin, Ger.P. 623,542 (1935).
81. Engelmann and Pikl, U.S.P. 2,304,156 (1942).
82. Engelmann and Pikl, U.S.P. 2,304,157 (1942).
83. Engelmann and Pikl, U.S.P. 2,313,741 (1943).
96. Färberei A.G., B.P. 477,029 (1937).
104. Färberei A.G., Ger.P. 687,907 (1940).
106. Färberei Gesellschaft Flores u. Co., Ger.P. 681,817 (1939).
111. Gault and Ehrmann, *Compt. Rend.* **177**, 124–7 (1923).
114. Grün, *Z. angew. Chem.* **34**, 645–8 (1921).
115. Guenther, Haussmann, and Alt, U.S.P. 2,150,968 (1939).
118. Haussmann, Meissner, and Zinke, U.S.P. 2,225,589 (1940).
119. Heberlein and Co. A.G., B.P. 313,616 (1928).
121. Hentrich and Hueter, U.S.P. 2,411,860 (1946).
124. Hubert and Heisenberg, Ger.P. 718,566 (1942).
128. I. G. Farben A.G., B.P. 441,016 (1936).
129. I. G. Farben A.G., B.P. 451,300 (1936).
130. I. G. Farben A.G., Fr.P. 801,919 (1936).
132. I. G. Farben A.G., Fr.P. 806,944 (1936).
134. I. G. Farben A.G., B.P. 460,602 (1937).
136. I. G. Farben A.G., B.P. 461,670 (1937).
140. I. G. Farben A.G., B.P. 467,992 (1937).
141. I. G. Farben A.G., Fr.P. 809,404 (1937).
145. I. G. Farben A.G., B.P. 479,753 (1938).
160. I. G. Farben A.G., Fr.P. 851,350 (1940).
161. I. G. Farben A.G., Fr.P. 851,904 (1940).
163. I. G. Farben A.G., Fr.P. 852,552 (1940).
166. I. G. Farben A.G., Ger.P. 711,292 (1941).
175. Kaase and Waltmann, U.S.P. 2,171,791 (1939).
184. Karrer, U.S.P. 1,897,026 (1933).
185. Kita, Sakurada, and Nakashima, *Cellulose Ind.* (Tokyo) **2**, 30–2 (1926).
186. Koreska Co., Wilhelm, Austrian P. 137,650 (1934).
188. Lant, Fr.P. 707,688 (1931).
189. Lant, B.P. 376,295 (1932).
190. Lant, U.S.P. 2,032,992 (1936).
191. Lant and Koreska, B.P. 343,104 (1929).
193. Little, "Flameproofing Textile Fabrics," A.C.S. Monograph No. 104, New York, Reinhold, 1937.
194. Lommel and Münzel, Ger.P. 722,481 (1942).
198. Maxwell, U.S.P. 2,293,844 (1942).
201. Moeller, B.P. 145,610 (1920).
202. Moeller, B.P. 145,611 (1921).
203. Moeller, Fr.P. 517,953 (1921); "Cellulose Verbindungen," Faust, p. 540.
204. Moeller, Swiss P. 94,856 (1922).
205. Moeller, B.P. 184,462 (1923).
206. Moeller, Canadian P. 229,826 (1923).
208. Moeller, Ger.P. 370,198 (1923).
209. Moeller, Norwegian P. 37,669 (1923).
210. Moeller, Swedish P. 58,826 (1923); "Cellulose Verbindungen," Faust, p. 541.
216. Moeller, U.S.P. 1,499,025 (1924).
217. Moncrief and Bates, U.S.P. 2,372,386 (1945).
221. Nathansohn, B.P. 355,256 (1929).
222. Nathansohn, Ger.P. 521,029 (1929).
223. Nathansohn, Ger.P. 542,186 (1929).
224. Nathansohn, Fr.P. 693,803 (1930).
225. Nathansohn, B.P. 356,878 (1931).
226. Nathansohn, Ger.P. 525,300 (1931).
227. Nathansohn, Ger.P. 554,874 (1931).
228. Nathansohn, Ger.P. 572,613 (1933).
229. Nathansohn, U.S.P. 2,092,702 (1937).
230. Nathansohn, U.S.P. 2,130,150 (1938).
235. Orthner, Balle, Rosenbach, and Bonstedt, U.S.P. 2,217,846 (1940).
236. Orthner, Balle, Rosenbach, and Bonstedt, U.S.P. 2,289,275 (1942).
237. Ott, "Cellulose and Cellulose Derivatives," New York, Interscience, 1943.
243. Pringsheim, Lorand, and Ward, *Celluloschem.* **13**, 119–27 (1932).
253. Rosenbach and Balle, U.S.P. 2,283,764 (1942).
259. Sauer, U.S.P. 2,268,169 (1941).
262. Sauer, U.S.P. 2,369,919 (1945).
271. Singer, Danish P. 55,494 (1938).
298. Studiengesellschaft für Faserveredelung m.b.H., Fr.P. 791,435 (1935).
301. Thomas and Kosolapoff, U.S.P. 2,401,440 (1946).
306. Ulrich and Koerding, U.S.P. 2,186,889 (1940).
316. Waltmann and Wolf, U.S.P. 2,297,731 (1942).

Part II. Quaternary Nitrogen Compounds

That the relative commercial success of the quaternary nitrogen type of water-repellent finish for cotton textiles has stimulated the search for the ideal agent in this class of organic compounds is manifested by the large number of these compounds which have been applied and patented. So many are the publications and patents which fall in this class that it has been found advantageous to make the following subdivisions: (1) alkoxymethyl quaternary compounds; (2) acylamidomethyl quaternary compounds; (3) alkyl quaternary compounds; (4) substituted phenyl methyl quaternary compounds; (5) *N*-carboalkoxy quaternary compounds; (6) miscellaneous quaternary compounds.

The most important sub-classes, because of commercial application, are the first two. In view of the large number of workers [38, 50, 55, 60, 187, 219, 220, 231, 238, 240, 272, 319] who have discussed the chemistry, application, and relative merits of this type, it will be useful to summarize here the supposed mechanism.

The original idea in the action of these types involved the instability of the pyridinium quaternary nitrogen in the presence of alkyl hydroxyl groups.

According to Mullin [219, 220] and others [38, 50, 55, 187] the chemistry involved was originally assumed to be as follows:

$$C_5H_5N(Cl)CH_2OC_{18}H_{37} \xrightarrow{CH_3COONa}$$

Octadecoxymethyl pyridinium chloride

$$C_5H_5N(OOCCH_3)CH_2OC_{18}H_{37} \xrightarrow{HOCell}$$

Octadecoxymethyl pyridinium acetate

$$C_5H_5N(OCell)CH_2OC_{18}H_{37} \xrightarrow{Heat}$$

Octadecoxymethyl pyridinium cellulose

$$C_{18}H_{37}OCH_2OCell + C_5H_5N$$

Octadecoxymethyl cellulose

or

$$C_5H_5N(Cl)CH_2NH{-}CO{-}C_{17}H_{35} \xrightarrow{CH_3COONa}$$

Stearamidomethyl pyridinium chloride

$$C_5H_5N(OOCCH_3)CH_2NH{-}COC_{17}H_{35} \xrightarrow{HOCell}$$

Stearamidomethyl pyridinium acetate

$$C_5H_5N(OCell)CH_2NH{-}COC_{17}H_{35} \xrightarrow{Heat}$$

Stearamidomethyl pyridinium cellulose

$$C_{17}H_{35}CO{-}NHCH_2OCell + C_5H_5N$$

Stearamidomethyl cellulose

According to Zerner and Pollak [332], the reaction may involve the formation of the quaternary ammonium hydroxide as an intermediate. Thus the following would happen:

$$C_{18}H_{37}OCH_2{-}C_5H_5N{-}OOCCH_3 \xrightarrow{H_2O}$$

Octadecoxymethyl pyridinium acetate

$$C_{18}H_{37}OCH_2{-}C_5H_5N{-}OH \xrightarrow{HOCell}$$

Octadecoxymethyl pyridinium hydroxide

$$C_{18}H_{37}OCH_2{-}C_5H_5N{-}OCell \xrightarrow{Heat}$$

Octadecoxymethyl pyridinium cellulose

$$C_{18}H_{37}OCH_2OCell + C_5H_5N$$

Octadecoxymethyl cellulose

A similar reaction without intermediates was used as an illustration in a French patent [97].

Davis [63] has made a substantial contribution to our knowledge of the reaction of stearamidomethyl pyridinium compounds with cotton. Working with commercial samples of a stearamidomethyl pyridinium type of compound, he obtained essentially pure stearamidomethyl pyridinium chloride (which he designates SAMPC) by successive extractions with water, cold acetone, and petroleum ether. The SAMPC, when boiled with water, simply hydrolyzed to methylolstearamide and pyridine hydrochloride as follows (R designates $C_{17}H_{35}$):

$$RCONHCH_2{-}C_5H_5N\cdot Cl + H_2O \longrightarrow RCONHCH_2OH + C_5H_5N\cdot HCl$$

On boiling the methylolamide with 5% sulfuric acid, the reaction first formed an ether and then split off formaldehyde as follows:

$$2\ RCONHCH_2OH \longrightarrow (RCONHCH_2)_2O \longrightarrow (RCONH)_2CH_2 + CH_2O$$

The distearamidomethane was unaffected by 5%

sulfuric acid, but could be hydrolyzed with 30% sulfuric acid to yield formaldehyde.

A method of estimating the quantity of SAMPC present on cloth by hydrolysis with 5% sulfuric acid, followed by determination of the formaldehyde liberated, was developed. It was considered that all SAMPC not chemically bound to the cellulose could be removed by extraction with boiling chloroform. From his results Davis tentatively concluded that when the application was less than 1% the stearamidomethyl pyridinium compound reacted entirely with the cellulose to yield:

$$RCONHCH_2OCell$$

For applications between 1% and 2% there was some methylolstearamide in loose association with the cloth in addition to the cellulose compound.

1. Alkoxymethyl Quaternary Compounds

In this group of quaternary compounds, about forty patents have been issued.

It should be borne in mind that the quaternary salts and related compounds have been used for some time for purposes other than for water-repellency—such as for animalization [51, 53, 67, 181, 182, 183, 296] or in improvement of color fastness [66, 67, 218, 263, 275, 276] and other properties [36].

One of the earliest of the *alkoxymethyl compounds* known is a product of the Imperial Chemical Industries, Ltd., and many of the patents reviewed here [8, 11, 87, 88, 89, 172, 245, 246] have been issued to this company.

A British Patent [64] described a preparation of this type through the following reaction:

$$C_5H_5N \cdot HCl + CH_2O + C_{18}H_{37}OH \longrightarrow C_5H_5N(Cl)CH_2OC_{18}H_{37}$$

Octadecoxymethyl pyridinium chloride

Reynolds, Walker, and Woolvin [167, 245, 246] have used *alkoxymethyl pyridinium chlorides* to obtain water-repellency. The process involves the solution of the compound in water and padding on cloth which is dried at low temperature and baked at about 90°C. Both natural and dyed cloth are used. The principal compounds employed are octadecoxymethyl pyridinium chloride and cetoxymethyl pyridinium chloride. The use of this type of compound on nylon has been patented by Imperial Chemical Industries Ltd. [75].

Baldwin, Reynolds, Walker, and Woolvin [11] have described a similar process. But instead of using previously prepared pyridine compound, these authors employed a process which involves its formation in the presence of the cloth. Thus, in the examples quoted, *chloromethyl alkoxy ethers* and pyridine are heated together in a solvent such as toluene. Cloth is then immersed and treatment is completed as before [245]. Besides pyridine, diethyl aniline is also used as the tertiary amine.

It should be pointed out that the processes described here do not exactly conform with the scheme outlined above for the reaction of alkoxy methyl pyridinium compounds with cellulose, since a buffering agent such as sodium acetate is not used. The reactions are:

$$C_5H_5N(Cl)OCH_2OC_{18}H_{37} \xrightarrow{HOCell}$$

Octadecoxymethyl pyridinium chloride

$$C_5H_5N(OCell)OCH_2OC_{18}H_{37} \xrightarrow{Heat}$$

Octadecoxymethyl pyridinium cellulose

$$C_{18}H_{37}OCH_2OCell + C_5H_5N$$

Octadecoxymethyl cellulose

or

$$C_5H_5N(Cl)OCH_2OC_{18}H_{37} \xrightarrow{H_2O}$$

Octadecoxymethyl pyridinium chloride

$$C_5H_5N(OH)OCH_2OC_{18}H_{37} \xrightarrow{HOCell}$$

Octadecoxymethyl pyridinium hydroxide

$$C_5H_5N(OCell)OCH_2OC_{18}H_{37} \xrightarrow{Heat}$$

Octadecoxymethyl pyridinium cellulose

$$C_{18}H_{37}OCH_2OCell + C_5H_5N$$

Octadecoxymethyl cellulose

In this process loss of strength by the textile material was not mentioned. The reaction is looked upon as harmless because the pyridine acts as an acid-binding agent.

As might be expected, many other types of alkoxymethyl compounds other than chlorides have been prepared and studied.

Baldwin and Piggott [8, 170] have reported the preparation of *alkoxymethyl pyridinium sulfites and pyrosulfites*. The preparation was accomplished by reactions similar to those given above. Long-chain alcohols, such as cetyl alcohol, were heated with

paraformaldehyde and pyridine. Sulfur dioxide was then passed through the mixture. The product was said to be a mixture of cetoxymethyl pyridinium pyridine sulfite and pyrosulfite. The reactions, which are probably based on the early work of Barnes, Harris, and Thomas [18], with pyridine and potassium sulfite, may take place as follows:

$$C_{16}H_{33}OH + CH_2O + C_5H_5N \longrightarrow$$

$$C_{16}H_{33}OCH_2{-}C_5H_5N{-}OH \xrightarrow{SO_2}$$

Cetoxymethyl pyridinium hydroxide

$$C_5H_5N(HOSO_2)CH_2OC_{16}H_{33} \xrightarrow{C_5H_5N}$$

Cetoxymethyl pyridinium hydrogen sulfite

$$C_{16}H_{33}OCH_2{-}C_5H_5N{-}OSO_2{-}C_5H_5N{-}H$$

Cetoxymethyl pyridinium pyridine sulfite

or

$$C_{16}H_{33}OH + CH_2O + C_5H_5N \longrightarrow$$

$$C_{16}H_{33}OCH_2{-}C_5H_5N{-}OH \xrightarrow{2\,SO_2}$$

Cetoxymethyl pyridinium hydroxide

$$C_{16}H_{33}OCH_2{-}C_5H_5N{-}OSO_2SO_2H \xrightarrow{C_5H_5N}$$

Cetoxymethyl pyridinium hydrogen pyrosulfite

$$C_{16}H_{33}OCH_2{-}C_5H_5N{-}OSO_2SO_2{-}C_5H_5N{-}H$$

Cetoxymethyl pyridinium pyridine pyrosulfite

Evans and Salkeld [89, 90, 91] have used the *alkoxymethyl pyridinium chlorides*, as well as several other types of quaternary compounds, in the presence of starch (wheat, tapioca, potato starch, etc.) in order to produce water-repellent starch finishes on cloth, yarns, paper, etc. The process is carried out in several ways. The cloth may be treated with starch first, then with the alkoxymethyl pyridinium compound, or it may be treated with a solution containing both the starch and the water-repellent agent. Another method described consists of mixing the dry starch with the water-repellent and dissolving the stock mixture. In addition to the pyridinium chlorides, these authors have used the pyridinium sulfites previously described, the acyl amido compounds to be discussed later, and pyridinium oxalates which were prepared as were the sulfites, with oxalic acid.

Patents granted to the Färberei A.G. [97, 99, 101, 107] describe the use of quaternary compounds similar to those already discussed and also [97, 101] *quaternary salts produced from long-chain alkoxymethyl isothiocyanates:*

$$C_{18}H_{37}OCH_2NCS + C_5H_5N \longrightarrow$$

Octadecoxymethyl isothiocyanate

$$C_{18}H_{37}OCH_2{-}C_5H_5N{-}NCS$$

Octadecoxymethyl pyridinium isothiocyanate

Also it is shown [97] that nitriles may be used for the production of quaternary salts of this type:

$$C_{17}H_{35}CN + CH_2O + HCl \longrightarrow$$

$$C_{17}H_{35}C(=NH)OCH_2Cl \xrightarrow{C_5H_5N}$$

α-imino-octadecoxymethyl chloride

$$C_{17}H_{35}C(=NH)OCH_2{-}C_5H_5N{-}Cl$$

α-imino-octadecoxymethyl pyridinium chloride

These compounds will be discussed elsewhere in this report. Methods of application were practically identical with those described above, involving dipping into aqueous solution, drying at approximately 45°C, and baking at 100°C.

It might be pointed out that the authors added sodium acetate when the pyridinium chlorides were used. This was not mentioned in the British patents discussed above, although one [245] states that wetting agents and buffers might be added to the bath.

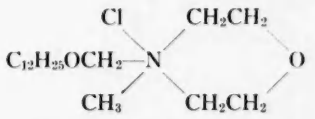
Patents issued to the I. G. Farbenindustrie A.G. [142, 149] describe the preparation and use of several more *complex alkoxymethyl quaternary salts*, many of which involve tertiary amines other than pyridine. Among the compounds given in the examples are:

$$C_{18}H_{37}OCH_2N(CH_3)_3Cl$$

Octadecoxymethyl trimethyl ammonium chloride

$$CH_2[N(Cl)(CH_3)_2CH_2OC_{18}H_{37}]_2$$

Bis(octadecoxymethyl dimethyl)-methylene diamine dichloride



Dodecoxymethyl methyl morpholinium chloride

$$C_{18}H_{37}OCH_2NCl(CH_3)_2CH_2CH_2OCH_3$$

Octadecoxymethyl-methoxyethyl-dimethyl ammonium chloride

$$C_{18}H_{37}OCH(CH_3)NCl(CH_3)_2C_6H_5$$

1-octadecoxyethyl-phenyl-dimethyl ammonium chloride

$C_{12}H_{25}—(p)C_6H_5—C_4H_8OCH_2NC_5H_5(Cl)$

4-(*p*-dodecylphenyl)butoxymethyl pyridinium chloride

It should be noted, too, that in all cases α-chlorides were used in the preparation.

The treatment of cloth (in most cases, rayon) with these compounds was essentially the same as that described for the simple octadecoxymethyl pyridinium chloride. In one instance, cloth was treated in an alcoholic solution of the quaternary salt containing the methylolamide of the acids derived from coconut oil. However, sometimes an elaborate pretreatment was used. In one case the cloth was first treated with alcoholic caustic solution (about 5%) and allowed to dry at room temperature. This was followed by a treatment with 1% ethylene oxide in carbon tetrachloride. As an after-treatment the cloth was dipped in a solution of aluminum acetate, wrung, and baked for 2 hours at 110°–120°C.

Another patent [143] describes the application of the same compounds listed in [142] to wool or other fibers of animal origin. The details of the treatment vary somewhat. Sometimes the pretreatment with ethylene oxide was used as described. Often, compounds such as methylol stearamide were used in conjunction with the quaternary compound. In all cases the material was baked at 100°–120°C for 1 to 2 hours.

Stühmer [300] has also used *halomethyl ethers of higher fatty alcohols*. No details are given except that aqueous solutions were used, and baking at 100°C was necessary. Similar compounds are also claimed by the Deutsche Hydrierwerke A.G. [64, 65].

Bock [32] describes the preparation of *aminomethyl ethers* by the reaction of primary or secondary alcohols with anhydrous formaldehyde (in the form of paraformaldehyde or trioxymethylene) and a non-aromatic ditertiary methylene diamine, usually in an organic solvent. The following will serve to illustrate the reaction:

$$2\ C_{18}H_{37}OH + CH_2O + CH_2[N(CH_3)_2]_2 \longrightarrow$$

Tetramethyl methylene diamine

$$2\ C_{18}H_{37}OCH_2N(CH_3)_2$$

Octadecoxymethyl dimethyl amine

$$HO(CH_2)_{10}OH + CH_2O + CH_2[N(CH_3)_2]_2 \longrightarrow (CH_3)_2NCH_2O(CH_2)_{10}OCH_2N(CH_3)_2$$

Bis-1,10-(dimethyl aminomethoxy) decane

The resulting amino ethers may be treated with alkylating agents such as methyl chloride, ethyl sulfate, benzyl chloride, allyl bromide, etc. to produce the corresponding quaternary salts.

Bock [29] also describes the production of *compounds containing two oxymethyl groups* by treating the same amino ethers with aliphatic oxymethyl halides. Thus:

$$C_{18}H_{37}OCH_2N(CH_3)_2 + CH_3OCH_2Cl \longrightarrow C_{18}H_{37}OCH_2N(Cl)(CH_2OCH_3)(CH_3)_2$$

Octadecoxymethyl-methoxymethyl-dimethyl-ammonium chloride

Flores and Essers [108] describe a process for the treatment of textiles with *long-chain aliphatic isocyanates* containing hetero atoms or groups of atoms in the alkyl radical for the formation of urethanes. The reaction is described as probably taking place as follows:

$$C_{18}H_{37}OCH_2NC_5H_5(Cl) \xrightarrow{KNCO} C_{18}H_{37}OCH_2NC_5H_5(NCO) \xrightarrow{Heat}$$

Octadecoxymethyl pyridinium isocyanate

$$C_{18}H_{37}OCH_2NCO \xrightarrow{HOCell}$$

Octadecoxymethyl isocyanate

$$C_{18}H_{37}OCH_2NH—COOCell$$

N-octadecoxymethyl cellulose carbamate

These authors utilized this material in conjunction with creaseproofing, using dimethylol urea and tartaric acid.

A British patent [100] describes the preparation and use of *pyridinium salts of acylamido methyl chloromethyl ethers*, which may be prepared according to the following scheme,

$$C_{18}H_{37}CONH_2 + CH_2O \longrightarrow C_{18}H_{37}CONHCH_2OH \xrightarrow{CH_2O}$$

Methylol stearamide

$$C_{18}H_{37}CONHCH_2OCH_2OH \xrightarrow{HCl}$$

Hydroxymethoxymethyl stearamide

$$C_{18}H_{37}CONHCH_2OCH_2Cl$$

Chloromethoxymethyl stearamide

and of *acylimidomethyl chloromethyl ethers*, which can be prepared as shown previously. The procedure was similar to that described for other treat-

ments, suitable buffers being used to prevent action of acids on the cloth. Impregnated cloth was dried at 40°C and baked for 5 minutes at 140°C.

Evans, Piggott, *et al.* [88, 167, 172] describe long-chain *alkoxymethyl pyridinium salts* other than chlorides, such as nitrate, sulfite, oxalate, etc., prepared and used as discussed previously.

Nüsslein and von Finck [233] describe a process involving the use of compounds like stearoxymethyl pyridinium chloride in conjunction with pre-formed vinyl-type polymer, prepared from long-chain vinyl compounds and maleic acid. Treatment was carried out by impregnating from organic solution, following the same general procedure.

Corteen and Wood [58, 304, 330] have found that the strength and wearing qualities of fabrics are increased by following the *alkoxymethyl pyridinium chloride* treatment by one with an alkaline swelling agent. The cloth was impregnated with the water-repellent, washed in an ammonium hydroxide wash, immersed first in a bath of wetting agent such as 0.25% solution of the sodium salt of sulfonated oleyl alcohol, and then in one of caustic soda or other swelling agent. The swelling agents used included sodium hydroxide, potassium hydroxide, and cuprammonium hydroxide.

A French patent [156] describes a process very similar to those discussed in [58, 142, 143, 304, 330]. Like these, the patent describes the use of *resins* such as dimethylol urea-tartaric acid, melamine-formaldehyde, etc. in conjunction with the water-repellent agent. The purpose is to produce water-repellent, creaseproof fabrics.

Bock [30] describes the preparation and use of *alkoxymethyl alkyl and alkylene ammonium halides* according to the following examples:

$$C_{16}H_{33}OCH_2Cl + C_6H_5CH_2N(CH_3)_2 \longrightarrow C_{16}H_{33}OCH_2NCl(CH_3)_2CH_2C_6H_5$$

Hexadecoxymethyl dimethyl benzyl ammonium chloride

$$C_{16}H_{33}OCH_2Cl + (CH_3)_2NCH_2C(CH_3)=CH_2 \longrightarrow C_{16}H_{33}OCH_2NCl(CH_3)_2CH_2C(CH_3)=CH_2$$

Hexadecoxymethyl dimethyl methallyl ammonium chloride

Cloth was immersed in aqueous solutions ranging from 1% to 10%, dried, and baked at 100° to 130°C.

Waltmann [308], in place of the chloromethyl ethers, has used *thiocyanomethyl ethers* produced by the reaction of chloromethyl ethers with potassium thiocyanate. When these were combined with pyridine, alkoxymethyl pyridinium thiocyanates were produced. Amines other than pyridine may be used. Cotton, wool, and rayon fabrics were each treated with a solution of the pyridinium compound in benzine or other organic solvent.

Waltmann [309, 312] has also developed a process for rendering cotton water-repellent which simultaneously animalizes the fiber so that it can be dyed with wool dyes or can be mixed with wool without greatly interfering with the dyeing process. This was accomplished by using water-repellents in which a free amino or imino group was left in the molecule after the material was fixed to the cloth. The compounds used by Waltmann were *quaternary iminoalkoxymethyl chlorides or quaternary alkylamino alkoxymethyl ammonium compounds*, which may be prepared as follows:

$$C_{17}H_{35}CN + CH_2O + HCl \longrightarrow C_{17}H_{35}C(=NH)OCH_2Cl \xrightarrow{C_5H_5N}$$

α-imino-octadecoxy methyl chloride

$$C_{17}H_{35}C(=NH)OCH_2NC_5H_5Cl$$

α-imino-octadecoxymethyl pyridinium chloride

$$CH_3(CH_2)_{15}CH=CH_2 + HOCl \longrightarrow CH_3(CH_2)_{15}CHClCH_2OH \xrightarrow{HN(C_2H_5)_2} CH_3(CH_2)_{15}CH(CH_2OH)N(C_2H_5)_2HCl$$

α-methylol heptadecyl diethyl ammonium chloride

α-methylol heptadecyl diethyl ammonium chloride can be further treated with trioxymethylene and hydrogen chloride to form an amino chloromethyl ether, thus:

$$CH_3(CH_2)_{15}CH(CH_2OH)N(C_2H_5)_2 \xrightarrow{CH_2O + HCl} CH_3(CH_2)_{15}CH(CH_2OCH_2Cl)N(C_2H_5)_2 \xrightarrow{(CH_3)_3N} CH_3(CH_2)_{15}CH[CH_2OCH_2N(CH_3)_3Cl]N(C_2H_5)_2$$

β-diethylamino-octadecoxymethyl-trimethyl ammonium chloride

Treatment was the same as for other alkoxymethyl compounds followed by standard drying procedure for wool.

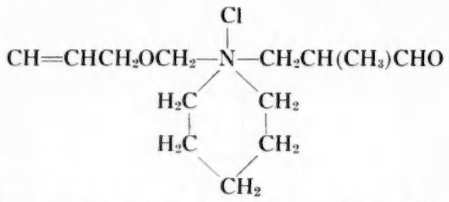
Waltmann [311] has also described the use of *alkoxymethyl and alkyl thiomethyl pyridinium compounds* with carbon chains of as many as 22 carbon atoms, in a manner similar to that already outlined.

Bock and Houk [35], using *aldehydo quaternary ammonium compounds*, give the preparation from α-disubstituted amino methyl aldehydes and halomethyl ethers as follows:

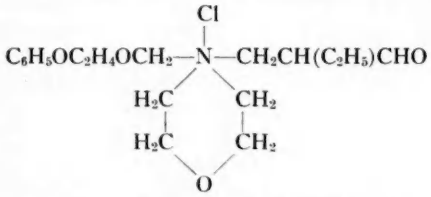
$$C_{18}H_{37}OCH_2Cl + (CH_3)_2NCH_2C(CH_3)_2CHO \longrightarrow C_{18}H_{37}OCH_2N(CH_3)_2ClCH_2C(CH_3)_2CHO$$

Octadecoxymethyl dimethyl (β-methyl-β-formyl)propyl ammonium chloride

Among other typical compounds prepared were:



Allyloxymethyl-β-formylpropyl piperidinium chloride



Phenoxyethoxymethyl-β-formylbutyl morpholinium chloride

$$CH_3OCH_2NBr(CH_3)(C_6H_{13})CH_2CH(CH_3)CHO$$

Methoxymethyl methyl cyclohexyl-β-formylpropyl ammonium bromide

Treatment to impart water-repellency consisted of impregnating the fabric and baking, as before.

2. Acylamidomethyl Quaternary Compounds

This second sub-class is nearly as large as the first. Again, the early patents were granted in Great Britain to Imperial Chemical Industries Ltd.

Baldwin and Walker [14, 15, 169] described the preparation of *quaternary ammonium salts* from acid amides as follows:

$$C_{17}H_{35}CONHCH_2OH + HCl + C_5H_5N \longrightarrow C_{17}H_{35}CONHCH_2NC_5H_5Cl$$

Stearamidomethyl pyridinium chloride

or

$$C_{17}H_{35}CONH_2 + CH_2O + C_5H_5N\cdot HCl \longrightarrow C_{17}H_{35}CONHCH_2NC_5H_5Cl$$

Many other examples are given which differ in the length of the carbon chain, or in the nature of the acid group connected to the tertiary nitrogen. The authors do not describe the use of these compounds for producing water-repellents but mention their utility in the treatment of textiles. Hartsfield and Richmond have patented the use of pastes of this type of compound [117]. Baldwin and Piggott [9] have prepared *N-alkyl acylamidomethyl quaternary compounds* by similar treatment of *N*-substituted amides.

Flores and Essers [110] have also described the preparation of *amido quaternary ammonium salts* by the reaction of the condensation product of trioxymethylene and *p*-toluenesulfonamide with stearyl chloride or octadecylchlorocarbonic acid ester and pyridine. They state that these compounds are useful in rendering textile fabrics water-repellent, but do not give details.

British patents [98, 313] granted to the Färberei Aktiengesellschaft describe the preparation of compounds said to render textiles permanently water-repellent, as follows:

(1). $C_{17}H_{35}CONH_2 + CH_2O + HCl \longrightarrow C_{17}H_{35}CONHCH_2Cl \xrightarrow{NC_5H_5} C_{17}H_{35}CONHCH_2NC_5H_5Cl$

Stearamidomethyl pyridinium chloride

(2). $C_{17}H_{35}CONHCONH_2 + CH_2O + C_5H_5N\cdot HCl \longrightarrow C_{17}H_{35}CONHCONHCH_2NC_5H_5Cl$

N-stearyl-*N'*-methyl pyridinium chloride-urea

(3). $C_{18}H_{37}OOCNH_2 + CH_2O + C_5H_5N\cdot HCl \longrightarrow C_{18}H_{37}OOCNHCH_2NC_5H_5Cl$

N-carbo-octadecoxyaminomethyl pyridinium chloride

(4). $C_{18}H_{37}CONHNH_2 + CH_2O + C_5H_5N\cdot HCl \longrightarrow C_{18}H_{37}CONHNHCH_2NC_5H_5Cl$

N-stearyl-*N'*-methylpyridinium chloride-hydrazine

No details of the treatment are given. Similar compounds are claimed by Waltmann and Wolf [317] and by Baldwin and Rogers [12].

Patents [154, 157] to the I. G. Farbenindustrie A.G. cover the preparation and use as water-repellents of compounds by the reaction of *amides, urea, thiourea derivatives, urethanes, or thiourethanes, with formaldehyde or its polymers and an aliphatic or aromatic dibasic acid* and pyridine. The reaction described by these authors might be said to take place as follows:

$$C_{12}H_{25}N(CH_3)CONH_2 + CH_2O \longrightarrow C_{12}H_{25}N(CH_3)CONHCH_2OH \xrightarrow{C_6H_4(o)C_2O_3} C_{12}H_{25}N(CH_3)CONHCH_2OOC{-}C_6H_4(o){-}COOH \xrightarrow{C_5H_5N} C_{12}H_{25}N(CH_3)CONHCH_2OOC{-}C_6H_4(o)CONC_5H_5OH$$

N-methyl-*N*-dodecyl-*N'*-methyl (chloropyridinium phthalate) urea

Examples are cited using many different urea derivatives and many dibasic acids such as diglycollic anhydride, succinic anhydride, etc. Treatment of cloth involves dipping into a 10% bath of the compound, centrifuging, and drying at 110°C. Similar compounds have been prepared by Cusa, Salkeld, and Walker [61, 62] using urea derivatives and carbamates.

Shipp [268, 269] described a process for making *quaternary ammonium salts*, as follows:

$$C_{17}H_{35}CONH_2 + CH_2O + HOAc + C_5H_5N \longrightarrow C_{17}H_{35}CONHCH_2NC_5H_5OAc$$

Stearamidomethyl pyridinium acetate

Many other examples were cited, using formic, citric, salicylic, and sulfanilic acids, etc. The treatment with these compounds, all water-soluble, consisted in the same principle—impregnation with 2% solution, drying, and baking for 20 minutes at 120°C. The finish was said to be permanent.

Patents [155, 159] granted to the I. G. Farbenindustrie A.G. describe compounds much the same as those discussed above. However, in these patents the *pyridinium compound of substituted acyl amides* was used, and one of the substituents on the nitrogen is required to have at least 2 carbon atoms and a halogen, thus:

$$C_{17}H_{35}CONHCH_2CH_2NC_5H_5Cl$$

β-stearamidoethyl pyridinium chloride

Again, these compounds are soluble in water. For the treatment of cloth, a 1% solution was prepared and sodium acetate was added. The cloth was impregnated, squeezed dry, and baked at 110°–120°C for 30 minutes.

The Du Pont Company [76, 196, 197] claimed the preparation of *alkylamidomethyl quaternary compounds* which were more easily soluble than those heretofore described. The modification was essentially the use of polytertiary amines instead of the monotertiary amines encountered so far; thus

$$C_{17}H_{35}CONHCH_2Cl + (CH_3)_2NC_2H_4N(CH_3)_2 \longrightarrow C_2H_4[NCl(CH_3)_2CH_2NHCOC_{17}H_{35}]_2$$

Ethylene-bis(dimethyl-stearamidomethyl-ammonium chloride)

These compounds greatly resemble those discussed previously and treatments were similar.

Wirth and Deese [323, 324] have described a process for preparing *quaternary ammonium compounds* of the general formula,

$$RCONHCH_2N(tertiary)—X$$

as described previously, frequently by carrying out the reaction in inert solvents or mixtures of solvents free from hydroxyl groups. The distinction lies in the possibility of preparing the quaternary salts without isolating any of the intermediates.

Evans and Salkeld [92] have applied *stearamidomethyl pyridinium chloride* to the animal fibers wool and silk as well as to artificial protein fibers. Evans [87] has used this type of compound in conjunction with creaseproofing. The treatment was the same as that described previously. Collins, Slowinske, and Smith [57] employed similar compounds with resins.

Henke and Pikl [120] pointed out that the preparation of acylamido quaternary compounds by the methods outlined above was not easy when the tertiary amine was aliphatic. Accordingly, they have described the details of two processes for making the compounds, one of which was carried out in an inert solvent, the other with none. They pointed out also that free tertiary base was not necessary for the reactions, in contradiction to what may be inferred from the previous discussion.

Baldwin, Evans, and Salkeld [4, 5, 6, 90, 171] describe the application of stearamido, oleylamido, lauramido, etc. methyl pyridinium salts. Although the methods in general were the same as before, the authors illustrated some differences in the details of the treatment.

Similar compounds containing the thiocyanate group were claimed by Pikl [242].

Bruson [46] has patented the preparation of similar compounds using secondary amines.

Bock [31] illustrated the preparation and application of *dimethylene quaternary ammonium salts* from chloromethyl ethers, as follows:

$$C_2H_5OCH_2Cl + C_{17}H_{35}CONHCH_2N(CH_3)_2 \longrightarrow C_{17}H_{35}CONHCH_2NCl(CH_3)_2CH_2OC_2H_5$$

Stearamidomethyl-ethoxymethyl-dimethyl-ammonium chloride

Other compounds similarly prepared were:

$$C_{17}H_{35}CONHCH_2NCl(CH_3)_2CH_2OC_4H_9$$

Stearamidomethyl-butoxymethyl-dimethyl-ammonium chloride

$CH_3CONHCH_2NCl(CH_3)_2CH_2OC_{18}H_{37}$

Acetamidomethyl-octadecoxymethyl-dimethyl ammonium chloride

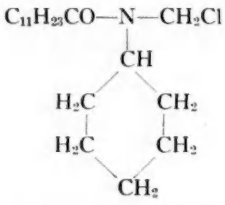
$C_{17}H_{35}CONHCH_2NCl(CH_3)_2CH_2OC_4H_9$

Oleylamidomethyl-butoxymethyl-dimethyl ammonium chloride

$C_{12}H_{25}OOCNHCH_2NCl(CH_3)_2CH_2OCH(CH_3)C_6H_{13}$

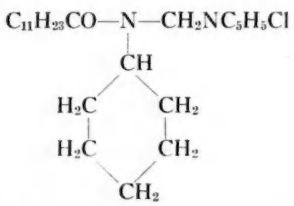
Dodecylcarbamidomethyl-2-octoxymethyl-dimethyl ammonium chloride

Baldwin and Piggott [7, 9, 10, 168] have described the preparation of the following types of compounds:



N-cyclohexyl-lauramidomethyl chloride

which, by methods previously described, may be converted to



N-cyclohexyl-lauramidomethyl pyridinium chloride

and

$CH_3OOCN(C_{17}H_{35})CH_2Cl$

N-carbomethoxyheptadecylaminomethyl chloride

which gives

$CH_3OOCN(C_{17}H_{35})CH_2NC_5H_5Cl$

These compounds were claimed by the authors to be good water-repellent agents for cotton and other cellulose compounds.

Wolf [327, 328] has also used *stearamidomethyl pyridinium chlorides*, making slight variations in the method of application. In addition he has described the preparation and use of similar compounds derived from montanic acid amide and from the amides of bicyclic naphthenic acids.

Wolf [102, 325, 326, 329] and Flores and Essers [109] prepared *quaternary ammonium compounds of the pyridine type* by the reaction of higher fatty acid chlorides with hexamethylenetetramine and pyridine. The reaction probably took place as follows:

$$4\ C_{17}H_{35}COCl + N_4(CH_2)_6 + 4\ NC_5H_5 \longrightarrow 2\ C_{17}H_{35}CONCH_2NC_5H_5Cl \mid CH_2 \mid C_{17}H_{35}CONCH_2NC_5H_5Cl$$

N-methylene-bis(stearamidomethyl pyridinium chloride)

Wolf also described the use of these compounds, which were water-soluble, for the treatment of cloth. This consisted again of impregnating with an aqueous solution, drying, and baking. It was claimed that these compounds were very suitable for use with anti-creasing preparations.

Rogers [248, 250] described the use of the pyridine compounds derived from di(*N*-chloromethyl-acylamido)methanes, prepared in the same manner as previously illustrated:

$$CH_2(HNCOC_{17}H_{35})_2 + 2\ HCl + 2\ CH_2O + 2\ NC_5H_5 \longrightarrow C_{17}H_{35}CONCH_2NC_5H_5Cl \mid CH_2 \mid C_{17}H_{35}CONCH_2NC_5H_5Cl$$

N-methylene-bis(stearamidomethyl pyridinium chloride)

Other compounds which Rogers described were:

$C_{17}H_{35}CONCH_2N(CH_3)_3Cl$

CH_2

$C_{17}H_{35}CONCH_2N(CH_3)_3Cl$

N-methylene-bis(stearamidomethyl-trimethyl-ammonium chloride)

$C_{17}H_{35}CONCH_2N(C_2H_5)_3Cl$

CH_2

$C_{17}H_{35}CONCH_2N(C_2H_5)_3Cl$

N-methylene-bis(stearamidomethyl-triethyl-ammonium chloride)

Treatment of material was as previously described, with baking at 140°C.

Sauer [260] has prepared *diacid amides*, which he converted to the corresponding pyridinium compounds, probably as follows:

$$2\ C_{17}H_{35}NH_2 + (CH_2)_4(COOH)_2 + 2\ HCl + 2\ CH_2O + 2\ NC_5H_5 \longrightarrow (CH_2)_4[CON(C_{17}H_{35})CH_2NC_5H_5Cl]_2$$

Di(heptadecyl-chloropyridiniummethyl) adipamide

Similar compounds were prepared using sebacic acid and dodecyl amine, yielding *N*,*N*′-di(dodecyl)

sebacamide. With triethyl amine the corresponding quaternary compound was produced. From aniline and tridecanoyl chloride followed by treatment with pyridine *N,N'*-(methylpyridinium chloride) *N,N'*-tridecane-dianilide was prepared. For use as a water-repellent the compounds were pasted with ethanol, and water and sodium acetate were added. Cloth was impregnated with this mixture, dried, and baked for 5 minutes at 150°C.

Swiss patents [288, 289, 290] granted to the Gesellschaft für Chemische Industrie in Basel describe the preparation of water-repellent compounds by the reaction of symmetrical *dichloro-dimethyl ether with long-chain amides* or substituted amides, and subsequent reaction with pyridine or other tertiary amine. For example:

$$C_{17}H_{35}CONH—C_6H_4(p)—CONH_2 + ClCH_2OCH_2Cl + NC_5H_5 \longrightarrow C_{17}H_{35}CONH—C_6H_4(p)—CONHCH_2OCH_2NC_5H_5Cl$$

p-stearamido-chloropyridiniummethoxymethyl benzamide

Rust [256, 257, 258] has used products prepared by the reaction of *long-chain nitriles with long-chain acid halides and formaldehyde* and a tertiary amine. A possible mechanism for the reaction is as follows:

$$C_{12}H_{25}CN + CH_2O + C_{15}H_{31}COCl + NC_5H_5 \longrightarrow C_{12}H_{25}C(=NH)OCH_2—NC_5H_5(OOCC_{15}H_{31})$$

α-imido-tridecoxymethyl pyridinium palmitate

Examples were given involving products from the following combinations: (1) stearonitrile with hexadecanoyl chloride or octadecanoyl chloride and quinoline, α-picoline, tributyl amine, or triethanolamine; (2) methyleneamino acetonitrile with stearyl chloride and the same amines. These products are water-soluble and may be used on cotton and other fabrics by methods already described. The baking treatment required temperatures from 120° to 170°C for 1 to 20 minutes.

Sauer [261] has patented the preparation of quaternary nitrogen compounds derived from amides which in turn have been derived from acyl ethanones (see also section on "ketenes," page 401). The preparation apparently follows these equations:

$$C_{17}H_{35}COC(C_{15}H_{31})=C=O + NH_3 \longrightarrow C_{17}H_{35}COC(C_{15}H_{31})HCONH_2 \xrightarrow{CH_2O + C_5H_5N\cdot HCl} C_{17}H_{35}COC(C_{15}H_{31})HCONHCH_2NC_5H_5Cl$$

α-stearyl-margaramidomethyl pyridinium chloride

Examples cited were:

$C_{16}H_{33}CH_2COCH(C_{16}H_{31})CONH_2$

α-stearyl stearamide

$C_{16}H_{33}CH_2COCH(C_{16}H_{33})CONHC_{10}H_{20}(5)OH$

α-stearyl-*N*-(5-hydroxydecyl)stearamide

The quaternary compounds were pasted with ethanol, water and sodium acetate were added, and the pH was adjusted to 5. Treatment was as usual, with baking at 150°C for 5 minutes.

MacKenzie [195] has patented the preparation of *quaternary nitrogen compounds containing silicon.* The preparation is similar to the methods used for compounds previously discussed:

$$2\ C_{17}H_{35}CONH_2 + SiCl_4 + 2\ CH_2O + 2\ NC_5H_5 \longrightarrow (C_{17}H_{35}CONH)_2Si(NC_5H_5Cl)_2$$

Distearamido-di-chloropyridinium-silane

The product was said to be water-soluble and capable of rendering textiles water-repellent when deposited and decomposed by heat.

3. Alkyl Quaternary Compounds

Although Bacon [3] has stated that, in general, for producing water-repellent effects the alkyl groups must be connected to the tertiary nitrogen atom by means of a noncarbon atom such as O, N, S, etc., a few patents covering the direct attachment of the alkyl radical to a quaternary nitrogen atom have been granted.

Linnhoff [192] has used the compounds of the general type R—N—Cl, including *lauryl, cetyl, stearyl, etc. pyridinium chlorides*, in conjunction with high acid anhydrides, such as the anhydrides of the acids from train oil (blubber). He claimed that a water-repellent finish resistant to boiling in water was produced upon boiling for 1 hour in an aqueous emulsion of the above mixture.

Götte [113] has also described the use of the same compounds. He claimed that such finishes may be produced by impregnation with a solution of octadecyl pyridinium chloride and then with a solution of the sodium salt of octadecyl sulfuric acid. The treatments were carried out at about 35°C for periods of 10 minutes, followed by drying. No baking was required. The finishes were said to be quite stable, withstanding several washes or wet treatments.

A British patent [37] to the H. T. Böhme A.G. described a treatment almost identical with those

outlined above. This, however, made use of two alkyl sulfates. The fabric was treated with a mixture of separately prepared solutions of octadecyl pyridinium chloride, hexadecyl hydrogen sulfate, and octadecyl hydrogen sulfate. It was then simply dried without rinsing or other after-treatment.

4. Substituted Phenylmethyl Quaternary Compounds

Phenyl compounds with one or more aliphatic groups on the benzene ring have been used to prepare water-repellents for textiles. Thus, Brunner [43, 170], Brunner and von Finck [44, 45], and the I. G. Farbenindustrie A.G. [144] have prepared *chloromethyl alkyl phenols* from which quaternary salts can be made. For example:

$$HO—C_6H_4(p)—isoC_8H_{17} + CH_2O + NC_5H_5 \cdot HCl \longrightarrow HO—C_6H_3—[(o)CH_2NC_5H_5Cl][(p)isoC_8H_{17}]$$

o-chloropyridiniummethyl-*p*-iso-octyl-phenol

A large variety of compounds of this type have been prepared, including the products from diiso-octyl phenol, isobutyl iso-octyl phenol, dodecyl phenol, isotridecyl phenol, isotetradecyl phenol, etc. and pyridine or other tertiary amines.

Two British patents [144, 146] and a French patent [150] are concerned with the preparation and application, respectively, of the phenyl type of compound described above. The compounds mentioned included the products from isobutyl phenol and chloromethyl dodecyl phenol combined with formaldehyde and hydrogen chloride, followed by pyridine or methyl pyridine.

For application, the cloth was padded with a solution made by dissolving the above pyridinium compounds in water and then dried and heated to about 120°C for about 20 minutes. These compounds were also used in conjunction with mixed polymeric materials such as those obtained from maleic acid and long-chain vinyl compounds.

Bruson and MacMullen [49] have prepared *phenolic triamines* by the reaction of phenol with secondary amines and formaldehyde:

$$C_6H_5OH + 3(CH_3)_2NH + 3\,CH_2O \longrightarrow HO—C_6H_2—(2,4,6)CH_2N(CH_3)_2$$

2,4,6-tri(dimethylaminomethyl)phenol

These can be combined with alkyl halides to form quaternary salts. Compounds from phenol and formaldehyde with morpholine, diethylamine, diethanol amine, piperidine, etc. have been prepared. The quaternary salts produced with the proper choice of alkyl halide were said by the authors to be good textile agents for waterproofing and fixatives for direct dyestuffs, as well as bactericidal agents. Bruson and Bock [47] have prepared similar compounds with alkyl chains on the ring.

Nüsslein and von Finck [233] have used compounds similar to those described by Brunner. In addition, these authors claimed to have produced even greater water-repellency by use of the compounds mentioned in combination with mixed *polymerizates from unsaturated carboxylic acids and olefins*, one of which has a long alkyl chain; as, for example, the polymer from maleic anhydride and vinyloctadecyl ether or maleic acid monomethyl ester and stearic acid vinyl ester. The process for treatment of cloth consisted in impregnating with an emulsion containing a polymeric product as described, with or without paraffin. After squeezing and drying, the cloth was again impregnated with a solution of the pyridinium salt of a phenolic compound as described by Brunner.

The Geigy A.G. has patented [112] the preparation and use of *quaternary compounds derived from substituted phenols*, of which the following are examples:

$$HO—C_6H_2—(2)COOH(4)CH_2OC_{18}H_{37}(6)CH_2Cl$$

2-carboxy-4-octadecoxymethyl-6-chloromethyl-phenol

$$CH_3O—C_6H_3—(2)CH_2Cl(4)CH_2OC_{18}H_{37}$$

2-chloromethoxy-4-octadecoxymethyl-anisole

5. *N*-Carboalkoxy Quaternary Compounds

This class of compounds is quite similar to the alkylamido compounds. The essential difference is that they have a carboalkoxy or carbamate group instead of the acyl group connected to the amino nitrogen.

Rogers [249, 251, 252] has patented several different types of *carboalkoxy compounds*, including:

1. Di-octadecyl *N*:*N*-di(*N'*-chloropyridinomethyl)-*m*-phenylene dicarbamate, using *m*-phenylene diamine
2. Di-octadecyl *N*:*N*-di(*N'*-chloropyridinomethyl)-*o*-phenylene dicarbamate
3. Di-octadecyl *N*:*N*-di(*N'*-chloro pyridinomethyl)-hexamethylene dicarbamate

4. Di-octadecyl *N*:*N*-di(*N'*-chloro-triethyl ammoniomethyl)-*m*-phenylene dicarbamate
5. Di-octadecyl *N*:*N*-di(*N'*-chloropyridinomethyl)-1,5-morpholine dicarbamate

The preparation of a typical compound can be carried out as follows:

$$2\ C_{18}H_{37}OCOCl + H_2N{-}C_6H_4(p)NH_2 \longrightarrow$$

$$C_{18}H_{37}OOCNH{-}C_6H_4(p)NHCOOC_{18}H_{37} \xrightarrow{2\ CH_2O + 2\ HCl}$$

$$C_{18}H_{37}OOCN(CH_2Cl){-}C_6H_4(p)N(CH_2Cl)COOC_{18}H_{37}$$

Dioctadecyl *N*:*N*-di-(*N'*-chloro-pyridinomethyl)-*p*-phenylene dicarbamate

Textiles may be treated with these compounds in the same manner as that described for the other quaternary salts. Sodium acetate is added to remove the hydrogen chloride. The compounds may be used with or without crease-resistant agents.

Battye, Candlin, *et al.* [20, 21] have described a process for simultaneous creaseproofing and waterproofing. These authors stated that they produced a water-repellent agent through the reaction of a *fatty urethane*, as follows:

$$C_{18}H_{37}OOCNH_2 + CH_2O + C_5H_5N\cdot HCl \longrightarrow$$

$$C_{18}H_{37}OOCNHCH_2NC_5H_5Cl$$

N-carbo-octadecoxyaminomethyl pyridinium chloride

The authors claimed that cloth may be rendered creaseproof and water-repellent by treating with a solution of the condensation product of urea with formaldehyde to which the above product or other quaternary ammonium salt has been added. Details of the treatment were the same as those previously described.

In addition to this work, carboalkoxy types which appear in many other references [4, 6, 9, 10, 31, 62, 87, 98, 155, 313] have been classified below under several other appropriate headings.

6. Miscellaneous Quaternary Compounds

Some compounds have been used for the purpose of making cloth water-repellent which do not fall into any of the preceding classes. These miscellaneous compounds are here described.

A French patent [162] to the I. G. Farbenindustrie A.G. describes the use of compounds such as:

$$Cl(C_2H_5)NC_5H_4{-}(2)N(C_{18}H_{37})COC_{15}H_{31}$$

α-(octadecyl palmitamido)-*N*-ethyl pyridinium chloride

These compounds, soluble in water, were used in the presence of sodium acetate in the usual manner.

Balle, Rosenbach, and Orthner [16, 17] have described the use of quaternary nitrogen salts of *derivatives from chloroacetic acid* with alkoxy compounds; for example:

$$C_{18}H_{37}OH + CH_2O \longrightarrow$$

$$C_{18}H_{37}OCH_2OH \xrightarrow{ClCH_2COOH + C_5H_5N}$$

$$C_{18}H_{37}OCH_2OOCCH_2NC_5H_5Cl$$

Octadecoxymethyl-(α-chloropyridinium)acetate

Among the variations of this type of compound were:

$$C_{12}H_{25}{-}C_6H_4(p)OOCN(C_2H_5)CH_2OOCCH_2N(CH_3)_3Cl$$

N-ethyl-*N*-carbo(*p*-dodecyl)phenoxy-methyl-(trimethylchloroammonium)acetate

$$C_{18}H_{37}SCH_2OOCN(CH_3)_3Cl$$

N-carbo-octadecylthiomethoxy-trimethyl ammonium chloride

$$C_{17}H_{35}CONHCH_2OOCCH_2NC_5H_5Cl$$

Stearamidomethyl-(α-chloropyridinium) acetate

As before, the compounds may be used in conjunction with creaseproofing preparations.

Bacon [3] has reviewed the general types of quaternary compounds which have been used, including those having

(A) *an isothiouronium radical* [152, 153, 155]:

$$C_{17}H_{35}CONHCH_2SC(NH_2){=}NH_2Cl$$

Stearylamidomethyl isothiourea hydrochloride

$$\begin{array}{c} C_{17}H_{35}CONCH_2SC(NH_2){=}NH_2Cl \\ | \\ CH_2 \\ | \\ C_{17}H_{35}CONCH_2SC(NH_2){=}NH_2Cl \end{array}$$

Bis-thiouronium derivative of bis-chloromethylene distearamido methane

(B) *a phosphonium group* [81]:

$$C_{17}H_{35}CONHCH_2PO(OH)_2$$

Stearamidomethyl phosphonic acid

(C) *ethers with water-soluble methanol derivatives* [83, 84]:

$$C_{17}H_{35}CONHCH_2OCH_2COOH$$

Stearamidomethyl ether of glycollic acid

$$C_{17}H_{35}CONHCH_2OCH_2PO(OH)_2$$

Stearamidomethoxymethyl phosphonic acid

The distinction in this patent lies in the specifications for concentration of solutions and pH.

Rust [255] has used compounds of the type:

$$C_{17}H_{35}COCl + CH_2O + NC_5H_5 \longrightarrow C_{17}H_{35}COOCH_2NC_5H_5Cl$$

Stearoxymethyl pyridinium chloride

$$C_{17}H_{35}COCl + CH_3CHO + NC_5H_5 \longrightarrow C_{17}H_{35}COOCH(CH_3)NC_5H_5Cl$$

β-stearoxyethyl pyridinium chloride

$$C_{17}H_{35}COOCH_2Cl + N(C_2H_4OH)_3 \longrightarrow C_{17}H_{35}COOCH_2N(C_2H_4OH)_3Cl$$

Stearoxymethyl triethanol ammonium chloride

These compounds are soluble in water and may be used as before to produce water-repellent finishes on cloth. Similar compounds were claimed by the Warwick Chemical Company [318]. The Gesellschaft für Chemische Industrie has patented [291] the product of the reaction between the chloromethyl ester of stearic acid and thiourea.

Coffman and Sauer [56] have made *disulfonamides having quaternary ammonium groups* as shown below:

$$2\,C_{18}H_{37}NH_2 + C_2H_4(SO_2Cl)_2 + 2\,CH_2O + 2\,HCl + 2\,NC_5H_5 \longrightarrow C_2H_4[SO_2N(C_{18}H_{37})CH_2NC_5H_5Cl]_2$$

Ethylene di(*N*-octadecyl-*N*-chloropyridinium methyl)sulfonamide

West [320, 321] described the preparation of a series of compounds of which the following is an example:

$$CO(NHCH_2OH)_2 + CH_3OH + C_{18}H_{37}OH \longrightarrow CH_3OCH_2NHCONHCH_2OC_{18}H_{37}$$

N-octadecoxymethyl-*N'*-methoxymethyl urea

This compound will react with pyridine hydrochloride to yield:

$$C_{18}H_{37}OCH_2NHCONHCH_2NC_5H_5Cl$$

N-octadecoxymethyl-*N'*-chloropyridiniummethyl urea

These compounds were said to be very good water-repellent agents.

Literature Cited

(Part II)

3. Bacon, U.S.P. 2,327,160 (1943).
4. Baldwin, Evans, and Salkeld, B.P. 477,991 (1938).
5. Baldwin, Evans, and Salkeld, U.S.P. 2,278,417 (1942).
6. Baldwin, Evans, and Salkeld, U.S.P. 2,278,418 (1942).
7. Baldwin and Piggott, B.P. 471,130 (1937).
8. Baldwin and Piggott, B.P. 475,119 (1937).
9. Baldwin and Piggott, U.S.P. 2,131,362 (1938).
10. Baldwin and Piggott, U.S.P. 2,303,191 (1942).
11. Baldwin, Reynolds, Walker, and Woolvin, B.P. 469,476 (1937).
12. Baldwin and Rogers, B.P. 517,632 (1940).
14. Baldwin and Walker, B.P. 475,170 (1937).
15. Baldwin and Walker, U.S.P. 2,146,392 (1939).
16. Balle, Rosenbach, and Orthner, U.S.P. 2,301,676 (1942).
17. Balle, Rosenbach, and Orthner, U.S.P. 2,426,293 (1947).
18. Barnes, Harris, and Thomas, B.P. 317,736 (1928).
20. Battye, Candlin, Tankard, Corteen, and Wood, B.P. 506,721 (1939).
21. Battye, Candlin, Tankard, Corteen, and Wood, B.P. 517,011 (1940).
29. Bock, U.S.P. 2,204,653 (1940).
30. Bock, U.S.P. 2,209,383 (1940).
31. Bock, U.S.P. 2,282,702 (1942).
32. Bock, U.S.P. 2,287,464 (1942).
35. Bock and Houk, U.S.P. 2,276,149 (1942).
36. Böhme, A.G., Fr.P. 770,235 (1934).
37. Böhme, A.G., B.P. 425,431 (1935).
38. Bonnet, *L'Ind. Text.* **57**, 219–20, 254–6 (1940).
43. Brunner, U.S.P. 2,180,791 (1939).
44. Brunner and von Finck, U.S.P. 2,234,363 (1941).
45. Brunner and von Finck, Ger.P. 727,400 (1942).
46. Bruson, U.S.P. 1,952,008 (1934).
47. Bruson and Bock, U.S.P. 2,257,088 (1941).
49. Bruson and MacMullen, U.S.P. 2,220,834 (1940).
50. Burnand, *Teintex* **4**, 27–33, 97–104, 155–63 (1939).
51. Chemische Fabrik vormals Sandoz, B.P. 284,358 (1927).
53. Chemische Fabrik vormals Sandoz, Ger.P. 462,090 (1928).
55. Chwala, A., *Melliand Textilber.* **19**, 905–10 (1938).
56. Coffman and Sauer, U.S.P. 2,362,886 (1944).
57. Collins, Slowinske, and Smith, U.S.P. 2,361,270 (1944).
58. Corteen and Wood, B.P. 506,783 (1939).
60. Croen, *Cotton* (Atlanta) **107**, 63–6 (1943).
61. Cusa, Salkeld, and Walker, B.P. 497,856 (1938).
62. Cusa, Salkeld, and Walker, B.P. 498,287 (1938).
63. Davis, *J. Soc. Dyers and Colourists* **63**, 260–3 (1947).
64. Deutsche Hydrierwerke A.G., B.P. 394,196 (1933).
65. Deutsche Hydrierwerke A.G., Fr.P. 743,594 (1933).
66. Deutsche Hydrierwerke A.G., Fr.P. 761,650 (1934).
67. Deutsche Hydrierwerke A.G., B.P. 426,482 (1935).
75. Dunbar, Landells, Norris, Smith, and Imperial Chemical Industries Ltd., B.P. 577,433 (1946).
76. du Pont, E. I., de Nemours and Co., B.P. 536,619 (1941).
81. Engelmann and Pikl, U.S.P. 2,304,156 (1942).
83. Engelmann and Pikl, U.S.P. 2,313,741 (1943).
84. Engelmann and Pikl, U.S.P. 2,313,742 (1943).

87. Evans, B.P. 501,288 (1939).
88. Evans, Piggott, Salkeld, Reynolds, Walker, and Woolvin, B.P. 495,025 (1938).
89. Evans and Salkeld, B.P. 472,389 (1937).
90. Evans and Salkeld, B.P. 493,920 (1938).
91. Evans and Salkeld, U.S.P. 2,125,901 (1938).
92. Evans and Salkeld, U.S.P. 2,250,930 (1941).
97. Färberei A.G., Fr.P. 819,945 (1937).
98. Färberei A.G., B.P. 492,699 (1938).
99. Färberei A.G., B.P. 493,067 (1938).
100. Färberei A.G., B.P. 494,761 (1938).
101. Färberei A.G., B.P. 494,833 (1938).
102. Färberei A.G., Fr.P. 834,949 (1938).
107. Färberei Gesellschaft Flores u. Co., Ger.P. 727,319 (1942).
108. Flores and Essers, B.P. 487,645 (1938).
109. Flores and Essers, B.P. 501,480 (1939).
110. Flores and Essers, B.P. 507,687 (1939).
112. Geigy, A.G., B.P. 553,681 (1934).
113. Götte, U.S.P. 2,051,843 (1936).
117. Hartsfield and Richmond, U.S.P. 2,419,399 (1947).
120. Henke and Pikl, U.S.P. 2,268,395 (1941).
142. I. G. Farben A.G., Fr.P. 822,195 (1937).
143. I. G. Farben A.G., Fr.P. 822, 196 (1937).
144. I. G. Farben A.G., B.P. 478,571 (1938).
146. I. G. Farben A.G., B.P. 489,495 (1938).
149. I. G. Farben A.G., B.P. 496,130 (1938).
150. I. G. Farben A.G., Fr.P. 832,029 (1938).
152. I. G. Farben A.G., B.P. 507,207 (1939).
153. I. G. Farben A.G., B.P. 507,628 (1939).
154. I. G. Farben A.G., B.P. 508,066 (1939).
155. I. G. Farben A.G., B.P. 511,144 (1939).
156. I. G. Farben A.G., Fr.P. 836,872 (1939).
157. I. G. Farben A.G., Fr.P. 847,824 (1939).
159. I. G. Farben A.G., Fr.P. 850,862 (1939).
162. I. G. Farben A.G., Fr.P. 852,372 (1940).
167. Imperial Chemical Industries Ltd., Fr.P. 816,387 (1937).
168. Imperial Chemical Industries Ltd., Fr.P. 818,438 (1937).
169. Imperial Chemical Industries Ltd., Fr.P. 821,856 (1937).
170. Imperial Chemical Industries Ltd., Fr.P. 821,857 (1937).
171. Imperial Chemical Industries Ltd., Fr.P. 822,787 (1938).
172. Imperial Chemical Industries Ltd., Fr.P. 836,069 (1939).
181. Karrer, B.P. 249,842 (1925).
182. Karrer, Ger.P. 438,324 (1926).
183. Karrer, B.P. 263,169 (1927).
187. Kursanov and Selkina, *J. Applied Chem.* (U.S.S.R.) **16**, 36–46 (1943).
192. Linnhoff, U.S.P. 2,270,658 (1942).
195. MacKenzie, U.S.P. 2,415,017 (1947).
196. Maxwell, B.P. 538,608 (1941).
197. Maxwell, U.S.P. 2,259,650 (1941).
218. Mullin, *Textile Colorist* **53**, 834–7 (1931).
219. Mullin, *Textile Colorist* **60**, 96–100, 163–6, 231–3 (1938).
220. Mullin, *Chem. Ind.* **47**, 404–9 (1940).
231. Norris, *Text. Mercury and Argus*, Jubilee Issue, **173–9** (1939).
233. Nüsslein and von Finck, U.S.P. 2,234,501 (1941).
234. Nüsslein, von Finck, and Stärk, U.S.P. 2,168,535 (1939).
238. Pascalis, *Tiba* **17**, 337–45 (1939).
240. Peters, *Rayon Text. Mo.* **19**, 167–8 (1938).
242. Pikl, U.S.P. 2,331,276 (1943).
245. Reynolds, Walker, and Woolvin, B.P. 466,817 (1937).
246. Reynolds, Walker, and Woolvin, U.S.P. 2,243,682 (1941).
248. Rogers, B.P. 517,474 (1940).
249. Rogers, B.P. 517,631 (1940).
250. Rogers, U.S.P. 2,386,140 (1945).
251. Rogers, U.S.P. 2,386,141 (1945).
252. Rogers, U.S.P. 2,386,142 (1945).
255. Rust, U.S.P. 2,261,097 (1941).
256. Rust, U.S.P. 2,285,948 (1942).
257. Rust, U.S.P. 2,315,135 (1943).
258. Rust, U.S.P. 2,333,623 (1943).
260. Sauer, U.S.P. 2,310,873 (1943).
261. Sauer, U.S.P. 2,323,938 (1943).
263. Schirm, Ger.P. 613,735 (1935).
268. Shipp, U.S.P. 2,146,408 (1939).
269. Shipp, U.S.P. 2,160,176 (1939).
272. Slowinske, *Cotton* (Atlanta) **105**, 67–70 (1941).
275. Society for the Chemical Industry in Basel, B.P. 390,553 (1933).
276. Society for the Chemical Industry in Basel, B.P. 396,992 (1933).
279. Society for the Chemical Industry in Basel, Swiss P. 203,947 (1939).
288. Society for the Chemical Industry in Basel, Swiss P. 213,559 (1941).
289. Society for the Chemical Industry in Basel, Swiss P. 213,560 (1941).
290. Society for the Chemical Industry in Basel, Swiss P. 213,561 (1941).
291. Society for the Chemical Industry in Basel, Swiss P. 214,541 (1941).
296. Stocker, U.S.P. 1,662,404 (1928).
300. Stühmer, Ger.P. 725,795 (1942).
304. Tootal Broadhurst Lee Co., Ltd., Fr.P. 842,580 (1939).
308. Waltmann, U.S.P. 2,220,856 (1940).
309. Waltmann, U.S.P. 2,264,490 (1941).
311. Waltmann, U.S.P. 2,277,174 (1942).
312. Waltmann, U.S.P. 2,288,868 (1942).
313. Waltmann and Wolf, B.P. 508,173 (1939).
317. Waltmann and Wolf, U.S.P. 2,380,133 (1945).
318. Warwick Chemical Co. and Clark, B.P. 560,448 (1944).
319. Wengraf and Schwarz, *Am. Dyestuff Reptr.* **31**, 551–8 (1942).
320. West, U.S.P. 2,344,934 (1944).
321. West, U.S.P. 2,397,451 (1946).
323. Wirth and Deese, U.S.P. 2,212,654 (1940).
324. Wirth and Deese, U.S.P. 2,291,519 (1942).
325. Wolf, Ger.P. 673,589 (1939).
326. Wolf, U.S.P. 2,242,565 (1941).
327. Wolf, U.S.P. 2,294,435 (1942).
328. Wolf, U.S.P. 2,296,412 (1942).
329. Wolf, U.S.P. 2,301,352 (1942).
330. Wood, U.S.P. 2,200,944 (1940).
332. Zerner and Pollak, TEXTILE RESEARCH **14**, 242–5 (1944).

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Taber Yarn-Sheet Abrasion Test*

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Abstract

A technique is described for the determination of yarn abrasion-resistance free from other wear factors such as flexibility, strength, elongation, and fabric construction. The procedure is based on a sheet of parallel yarns wound under controlled tension and subsequently abraded to failure on a Taber Abraser. The method has been used to evaluate the effect of yarn properties as well as fiber type on yarn abrasion-resistance. Results on yarns correlate well with the Taber abrasion-resistance of fabrics made from these yarns, and can be used to determine the inherent yarn abrasion-resistance without the necessitiy of fabric preparation.

THE GENERAL PROBLEM of evaluating the wear-resistance of textiles has received considerable attention both in the United States and other countries [4, 5, 6, 7, 14, 15]. In virtually all cases it has been necessary to conduct field tests in end uses to obtain information on wear, because of the difficulty in correlating data observed in the laboratory with wear observed in service. This difficulty probably resides in the fact that wear is a composite result involving abrasion, flexing, strength, elongation, and other factors, all exerting their individual effects simultaneously, and it is almost impossible to set up a laboratory test which will include all of these factors at the same time and to the proper extent. One of the most important of the factors contributing to wear is believed to be abrasion, and it has seemed desirable to measure this property free from other factors affecting wear and thereby to contribute to the understanding of the more general problem.

Abrasion-testing has usually been confined to fabrics, which in turn are relatively complex structures, which makes tests inconvenient to carry out and difficult to understand. A test applicable to yarns would be accordingly quite desirable. Testers for this purpose have been described by Walker and Olmstead [16] and by Matthes and Keworkian [11]. These testers, however, do not measure abrasion free from other factors but, rather, measure a combination of abrasion-resistance and other properties such as flexibility and strength, and are unsatisfactory for this reason. Hamburger and Lee [8] developed a test which presumably meaures simple abrasion of yarns. They used a sheet of parallel yarns wound under controlled tension on a panel which could be abraded on a Taber Abraser. The preparation of the yarn sheet was comparatively simple and the sample comprising a number of ends was more representative than single-end tests. Relative abrasion-resistance was calculated as a "durability coefficient" obtained by determining loss in yarn strength after progressive degrees of abrasion on a succession of samples. It is accordingly a comparatively long and expensive test.

It was the purpose of this work to develop a rapid yarn abrasion test which would not be influenced by other wear factors and to use this test to evaluate the effect of yarn properties on abrasion-resistance. The procedure was similar to that described by Hamburger [8] except that the yarn was worn to failure, thereby eliminating the extensive work required to determine a "durability coefficient." The test gives sufficiently reproducible results and has been used to determine the effect of such properties as total denier, denier per filament, and twist, as well as fiber type, on yarn abrasion. The test is referred to as a "Taber yarn-sheet abrasion test."

Yarns Tested

The yarns used in the development of the test and in the evaluation of various factors affecting yarn abrasion are listed in Table I.

* Presented before the Fiber Society at Princeton, N. J., September, 1947, and also before the A.S.T.M. Committee D–13, special task group working on abrasion, at Philadelphia, October, 1947.

TABLE I. TEST YARNS

Yarn type	Production	Luster	Conditioned Tenacity (g./den.)	Conditioned Elongation (%)
A. Viscose rayon				
-1 Normal tenacity—filament *	Commercial	Bright	1.9	19
-2 Normal tenacity—filament	Commercial	Dull	1.8	17
-3 Medium-high tenacity—filament *	Experimental	Bright	2.7	18
-4 Normal tenacity—spun yarn	Experimental †	Bright	1.5	13
B. Acetate rayon				
Normal tenacity—filament *	Commercial	Bright	1.4	28
C. Fiber G rayon				
Filament	Experimental	Bright	4.8	6
D. Polyacrylonitrile				
Filament	Experimental	Bright	4.3	18
E. Nylon				
Filament *	Commercial	Bright	5.5	25

* Several varieties of these yarns were used to obtain a range of yarn numbers (deniers), denier-per-filament sections, or twists.

† This yarn was spun in an experimental unit from commercial 1.5-denier, 1.5-inch staple.

Method of Preparing Specimens and Test Procedures

A. Winding of Yarn Sheets

Yarn-sheet specimens were wound in serigraph fashion on a cardboard disc cut to fit the turntable of a Taber Abraser. Notches in the disc, as indicated in Figure 1, allowed the yarn sheet to be laid down in sections, part parallel and part perpendicular to the path of the abrasive wheel. The notched card was faced on one side with a standard resilient rubber pad as a specimen backing and on the other side with an abrasive cloth to prevent shifting of yarn on the sample disc. The yarn was wound under constant tension, by hand at first, and later with a mechanical winding device.

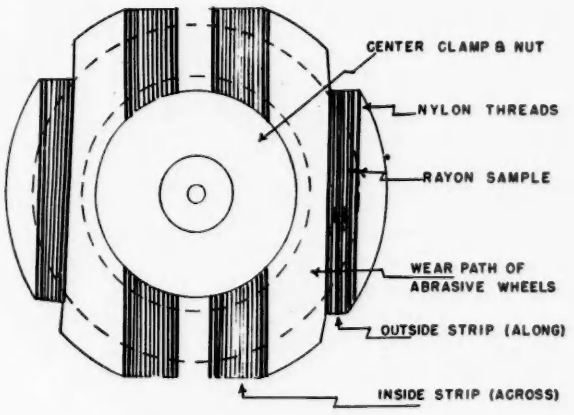

FIG. 1. *Arrangement of sample for Taber yarn-sheet abrasion test.*

In the original tests it was observed that, for any one band, the yarn at the edge which was first touched by the abrading wheel invariably broke first. It was concluded that this outside yarn had to absorb the energy necessary to lift the wheels from the plane of the table to the plane of the yarn sheet and that this was responsible for its comparatively early failure. Various materials have been tried for protecting the edge yarn and the best material found to date is nylon yarn of approximately the same denier. On the basis of this observation, three turns of nylon yarn were wound at each edge of each of the yarn sheets (Figure 1).

B. Determination of the End Point

The failure of a single end of yarn has been chosen to indicate the end point for a yarn group; thus two end points are obtained for the outside sheets, where the wheels are moving along the yarns. These values are materially lower than the four end points obtained for the inside sheets, where the abrasive wheels move across (essentially perpendicular to) the yarns.

Examination of the broken ends also indicated a difference in the structural breakdown of the yarns and the two types of end points have accordingly been carefully distinguished. The average of the breaks with the wear along the fibers has been noted separately from the average of the breaks with the wear across the fibers.

TABLE II. INFLUENCE OF TENSION ON TABER YARN-SHEET ABRASION LIFE

150–60 S 2.5 Viscose Rayon Yarn (A-3)*				
	Abrasion life (cycles)			
	CS-10 wheels, 500-g. load		CS-10 wheels, 250-g. load	
Tension (g./den.)	Along	Across	Along	Across
0.03	20	70	5	45
0.07	30	80	15	160
0.10	35	120	20	365
0.20	30	85	15	170

* See Table I for further details of yarn properties.

Investigation of Factors Influencing the Yarn-Sheet Abrasion Test

Reports of other workers [1, 2, 3, 9, 10, 12, 13, 15] using the Taber Yarn Abraser for testing fabrics indicated that relatively large variations in abrasion-resistance could be obtained by varying different parameters of the test such as tension of the specimen, load on the wheels, grade of the wheels, and variability within a wheel grade. Preliminary tests in our laboratory showed that these factors were equally important in yarn testing and data were obtained on each variable in order to set up a standard test procedure.

A. Influence of Tension on the Specimen

Tests were made in which a yarn was wound under a series of tensions ranging from 0.03 to 0.20 gram per denier and tested with different loads. The data are given in Table II. It is seen that the abrasion life first increases, then decreases. A tension value of 0.10 gram per denier was chosen as standard since this gave relatively high readings with a consequent increase in precision.

B. Load on Wheels

The pressure with which the abradant is applied to the sample on the Taber Abraser, is controlled by the load on the wheels. It was found that this pressure or load on the wheels had a marked influence on the abrasion life as measured in the Taber yarn-sheet test. Table III gives typical results for various types of yarn.

A load on the abrasion wheels of 250 grams was chosen as standard because (1) with the low load of 125 grams the tests were comparatively long and the wheels tended to bounce on the turntable, resulting in poor reproducibility; (2) the results obtained with the higher load of 500 grams did not have adequate precision because of the relatively great variability of the comparatively low values.

C. Grade of Wheel (CS-10 vs. CS-8)

The character of the abrasive used in an abrasion test influences strongly the abrasion life of the sample being tested [10, 11]. In the case of the Taber instrument, certain standard "Calibrase" wheels are available for abrading fabric. CS-8 wheels were compared with the CS-10 grade. The data, given in Table IV, show that the nature of the abradant definitely influences the observed level of results for abrasion life, particularly in the crosswise direction. It is also apparent that the relative difference varies with the type of sample.

To speed up the running of the yarn-sheet test and to take advantage of the fact that the CS-10 wheel appeared to give a superior reproducibility, the CS-10 Calibrase wheel was chosen as the standard for the Taber yarn-sheet test.

D. The Variation Within a Given Grade of Wheel

Variation in a series of wheels within a grade which has been reported in work with fabrics was found to hold also for yarns, as is seen from the results in Table V.

To avoid the influence of variations of this type it has been our practice to calibrate each wheel against a standard yarn and apply the necessary corrections to all subsequent observations made with the specific wheel.

TABLE III. INFLUENCE OF LOAD ON WHEELS UPON TABER YARN-SHEET ABRASION LIFE

	Abrasion life (cycles)					
Load (g.)	150–60 S 2.5 (A-3)*		150–40 S 2.5 (A-1)*		125–40 S 2.5 (A-2)*	
	Along	Across	Along	Across	Along	Across
125	125	1200	325	775	260	2125
250	60	750	75	300	55	200
500	20	85	25	75	50	70

* See Table I for further details of yarn properties.

TABLE IV. INFLUENCE OF GRADE OF WHEEL UPON ABRASION LIFE

Yarn	Average abrasion life (cycles)* CS-10 wheels Along	CS-10 wheels Across	CS-8 wheels Along	CS-8 wheels Across
Viscose rayon (A-1)	20	180	25	875
Fiber G rayon (C)	25	550	40	825
Acetate rayon (B)	10	95	10	140

* 500-gram load.

TABLE V. VARIATION IN CS-10 CALIBRASE WHEELS

CS-10 Wheels, 250-g. Load, 0.10 g./den. Tension
150–60 S 7 Viscose Rayon Yarn (A-1)

Wheels	Average abrasion life (cycles) Along	Across
CS-10-C	15	120
CS-10-D	20	180
CS-10-E	35	300
CS-10-G	30	220
CS-10-H	25	250
CS-10-J	25	140

Reproducibility of Yarn-Sheet Abrasion Test Results

The variation encountered in running a series of tests using the standard conditions discussed in the previous sections is shown by the data in Table VI. A coefficient of variation in the range of 10 to 15 was found for most samples. This is adequate to obtain comparative ratings when it is desired to compare experimental yarns.

It is seen that the reproducibility of the Taber yarn-sheet abrasion test is quite satisfactory for distinguishing between specimens showing a difference of 25 to 50 per cent. Smaller differences are believed to be without significance and are customarily disregarded in abrasion-testing.

Nature of Abrasive Wear

As has been indicated in each table, end points have been recorded for abrasion parallel to the yarn and for abrasion across the yarn. Since the abrasion-resistance of any given yarn appeared to differ considerably, depending on the direction of abrasive action, a study was undertaken to determine the nature of abrasive wear occurring under the two conditions. It was further desired to find out which, if either, of these two types of abrasion was similar to that obtained in the abrasion of fabric by the Taber Abraser.

Microscopic study of abraded samples indicated a definite difference in the nature of the abrasive action when the wheel traveled along the yarn as compared to the action when it traveled across the yarn. In the case of abrasion along the yarn, filaments were broken rather cleanly, with no progres-

TABLE VI. REPRODUCIBILITY OF TABER YARN-SHEET ABRASION TEST

150–60 S 3 Yarns, CS-10 Wheels, 500-g. Load, 0.10 g./den. Tension

Yarn	Average abrasion life Along	Across	Standard deviation* Along	Across	Coefficient of variation (%) Along	Across
Viscose rayon (A-1)	20	55	2.4	5.7	13	10
Acetate rayon (B)	10	50	1.4	17.2	14	33
Polyacrylonitrile (D)	60	155	5.7	18.3	10	12
Viscose rayon (A-3)	—	90	—	13.6	—	15
Fiber G rayon (C)	—	170	—	23.6	—	14

* Standard deviation values are based on 7 to 9 tests.

TABLE VII. ABRASION-RESISTANCE OF FILAMENT YARNS MADE FROM VARIOUS FIBERS

Yarn	Abrasion Across 150–60 S 3 Yarn, 0.10 g./den. Tension CS-10-B 500 g.	CS-10-A 250 g.	CS-10-A 500 g.	CS-10-E 500 g.	Rating
Acetate rayon (B)	50	625	70	35	75
Viscose rayon (A-1)	55	675	140	50	100
Viscose rayon (A-3)	90	850	170	85	150
Fiber G rayon (C)	170	1125	350	160	250
Polyacrylonitrile (D)	150	1350	400		275
Nylon* (E)		2000		1000	1000

* 210–68 S 0.7.

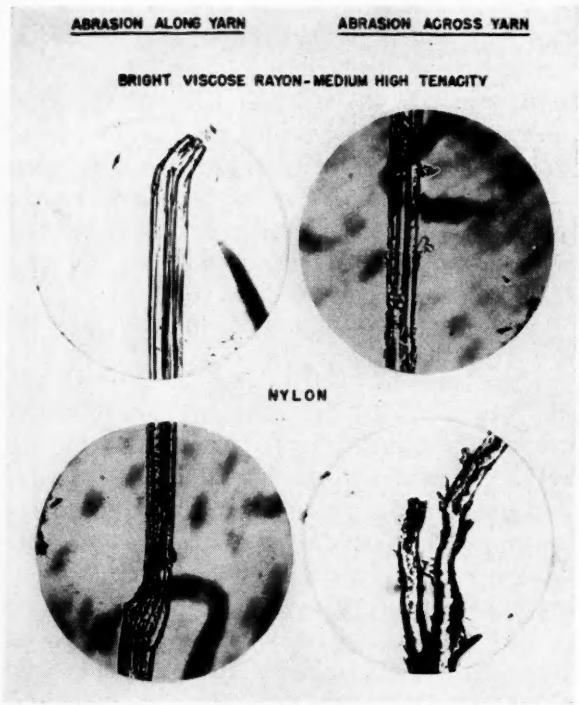

FIG. 2. *Abraded samples from Taber yarn-sheet abrasion test.*

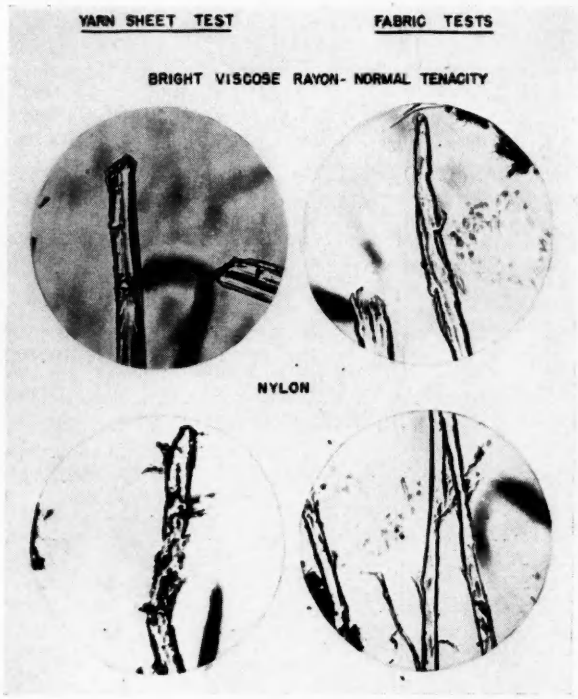

FIG. 3. *Abraded samples from Taber yarn and fabric abrasion test.*

sive abrasive wear. On the other hand, when abrasion was carried out across the yarn, progressive deterioration of individual filaments appeared to occur, with the final failure occurring at these weakened points. The photomicrographs in Figure 2 illustrate this behavior. The progressive abrasion or attrition of the fibers is particularly evident in the case of the viscose and nylon yarns for abrasion across the yarn.

Comparison of these samples of abraded yarn with those removed from fabric which had been abraded with the Taber instrument revealed that the appearance of yarn specimens from the fabric was very similar to that of yarns which were abraded with the wheels passing across the sheet (perpendicular to the fiber axis). As may be seen in Figure 3, abrasion of fabric occurs by the attrition of individual filaments. This mechanism of degradation is the same as that noted above for abrasion across the yarn sheet. In light of this observation and because of the fact that in general the abrasion across the yarn was more reproducible, the end point for abrasion across the yarn has been selected for characterizing yarns in this study.

Effect of Fiber and Yarn Structure on Abrasion

The test procedure discussed above was used to evaluate different fiber types and also to determine the effect of certain variables such as yarn number and yarn construction which have been thought to influence tests on fabric and on end-use serviceability [8].

A. Effect of Fiber Type

The Taber yarn-sheet test gave a very consistent rank rating to various types of continuous-filament yarn. The results, which are summarized in Table VII, indicate that the items increased in abrasion-resistance in the following order: acetate rayon, normal viscose rayon, medium-high-tenacity viscose rayon, Fiber G rayon, polyacrylonitrile yarns, and nylon.

B. Effect of Linear Density (Denier)

Total denier has been found to have a definite influence upon abrasion life as measured by the yarn-sheet test, an increase in denier resulting in a corresponding increase in abrasion-resistance. Table VIII summarizes this effect of denier for a series

TABLE VIII. INFLUENCE OF TOTAL DENIER ON ABRASION LIFE

Viscose Rayon Yarn S 2.5 Twist, 2.5 Denier/Filament (A-1)
CS-8 Wheels, 250-g. Load, 0.10 g./den. Tension

Denier	Average abrasion life (cycles) Across
50	160
75	210
150	220
300	350

of bright textile viscose rayon yarns of the same denier per filament. This increase in abrasion life with increased denier is thought to be due to the effectively larger number of filaments which must be abraded before failure of a single yarn occurs in a given yarn sheet. These results for the influence of denier agree well with general experience, which has shown the abrasion-resistance of fabrics made from coarser yarn to be considerably greater than that of fabrics made from finer yarn.

C. Effect of Denier Per Filament

As in the case of total denier, filament denier has a marked influence upon the abrasion-resistance of a yarn. Data are given in Tables IX and X. The data show that an increase in the size of the individual filaments results in a considerable increase in abrasion-resistance. It is also indicated that this relationship appears to level off at a value for a filament denier between 3 and 5. Again these results are in line with normal experience for the influence of filament denier upon the abrasion-resistance of yarn in end uses, which indicates that fine-filament yarns have poorer wearing properties than coarser-filament yarns.

TABLE IX. 150 S 1.8 VISCOSE RAYON (A-3)

250-g. Load, 30-g. Tension

Yarn No. Denier-Filament	Den./Fil.	Abrasion life—across (cycles) CS-8	CS-10
150–120	1.25	189	118
150–100	1.30	201	139
150–90	1.66	—	163
150–75	2.00	225	190
150–60	2.50	244	198
150–40	3.75	256	216

TABLE X. 150 S 2.5 VISCOSE RAYON (A-1)

250-g. Load, 30-g. Tension

Yarn No. Denier-Filament	Den./Fil.	Abrasion life—across (cycles) CS-8	CS-10
150–90	1.66	190	146
150–75	2.00	225	180
150–60	2.50	260	203
150–40	3.75	274	208

D. Effect of Twist

The influence of twist upon abrasion-resistance is more complicated than that of denier or denier per filament. As is seen from Figures 4 and 5, abrasion-

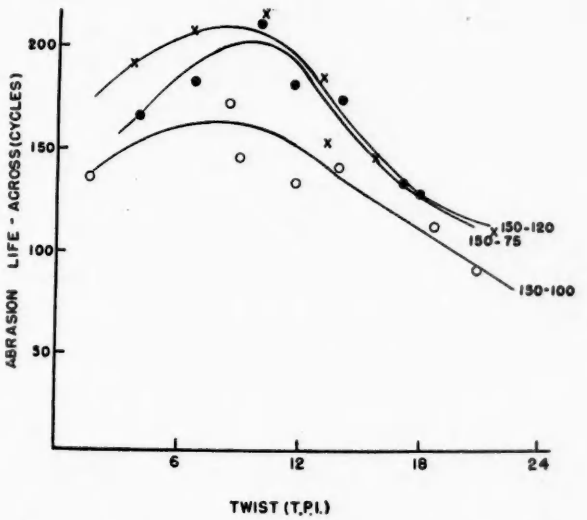

FIG. 4. *Influence of twist on Taber yarn-sheet abrasion life. 150-denier bright viscose rayon—medium-high tenacity; 250-g. load; 30 g. tension; CS–10 wheels.*

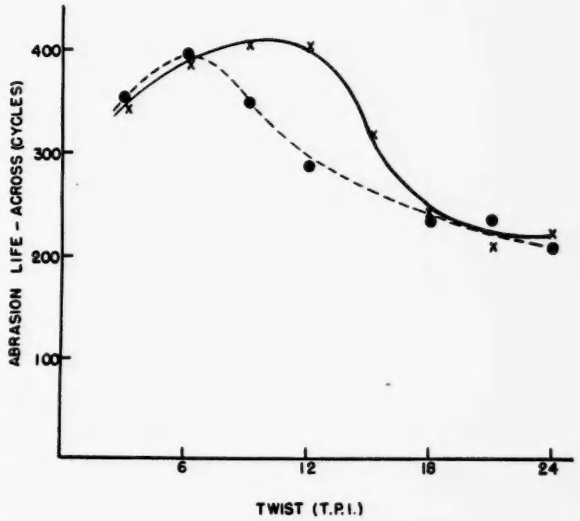

FIG. 5. *Influence of twist on Taber yarn-sheet abrasion life. 150–40, 2.5 S bright viscose rayon—normal tenacity; CS–10–D wheels; 250-g. load.*

TABLE XI. ABRASION RESISTANCE OF SPUN YARNS

Viscose Rayon Yarns, 0.10 g./den. Tension

Yarn	Abrasion life (cycles) CS-10, 500 g. Along	CS-10, 500 g. Across	CS-8, 250 g. Along	CS-8, 250 g. Across	Rating
Viscose, spun, 1.5 den./fil. (A-4)	15	30	30	35	30
Viscose, continuous filament, 2.5 den./fil. (A-1)	30	120	75	325	100*

* Corrected to 1.5-denier-per-filament basis.

resistance passes through a maximum with increasing twist, the point of maximum abrasion-resistance occurring in the range of 6 to 12 turns per inch for 150-denier yarn. This behavior appears to apply to both of the viscose yarns tested and may be assumed to be a general effect. The decrease in abrasion-resistance at low twist is thought to be due to the ease of snagging or picking filaments which are only loosely intertwined with the other filaments. The decreasing abrasion-resistance at the higher twists may be due to an increasing component in the direction of the wheel path, resulting in a somewhat more pronounced abrasion.

E. Effect of Filament Yarn vs. Spun Rayon Yarn

A comparison of a spun yarn with filament yarn indicated that the latter has greater abrasion-resistance. The results given in Table XI for two different sets of conditions established this order for typical viscose productions. The yarns used were a rayon filament of 150 denier (166 Grex) and a 40/1 spun rayon yarn (148 Grex).

Comparison of Yarn Abrasion with Fabric Abrasion

Although it would be desirable to evaluate the Taber yarn-sheet abrasion test in terms of actual wear, such a comparison could not be made because of the lack of field test data. However, comparison of yarn-sheet test results was made with the abrasion-resistance measurements obtained in Taber fabric abrasion tests. In view of the fact that the nature of the abrasion appeared to be similar for the yarn and fabric tests, as indicated earlier, it was anticipated that ratings by the two tests would be similar.

Application of the Taber yarn-sheet and Taber fabric abrasion tests to a variety of samples has indicated good correlation for the two methods in all cases in which composite (homogeneous) fabrics are used. Data are given in Table XII.

TABLE XII

Item	Abrasion-resistance rating Yarn	Fabric
Acetate rayon (B)	75	70
Viscose rayon (A-1)	100	100
Viscose rayon (A-3)	150	110
Fiber G rayon (C)	250	125
Polyacrylonitrile (D)	275	140
Nylon (E)	1,000	750

Yarn: 150 denier
Yarn test: CS-10 wheels, 250- and 500-g. loads, 0.1 g./den. tension
Fabric: 100 and 150 denier in plain weave (140 × 76)
Fabric test: CS-10 wheels, 500-g. load

Item	Abrasion-resistance Yarn Cycles	Yarn Rating	Fabric Cycles	Fabric Rating
Acetate rayon (B)	35	50	325	70
Viscose rayon (A-1)	70	100	475	100
Nylon (E)	400	575	3,700	775

Yarn: 75 denier
Yarn test: CS-10 wheel, 250-g. load, 0.1 g./den. tension
Fabric: 75-denier 5-shaft satin (250 × 180)
Fabric test: CS-10 wheels, 500-g. load

The data in the first part of Table XII suggest that for a given group of items the Taber yarn-sheet abrasion test gives a slightly greater range in abrasion-resistance ratings than does the Taber fabric abrasion test. This behavior is attributed to the fact that the complications of fabric construction tend to mask the influence of the inherent abrasion-resistance of the yarns themselves. This observation emphasizes the desirability of employing a yarn abrasion test as a screening test in work directed at improving inherent yarn abrasion-resistance. By use of such a method, the variables of fabric construction and processing may be removed from the abrasion-resistance measurement and the cost and time of preparing fabric for testing may be eliminated or materially reduced.

Summary

A modified Taber abrasion test on yarns instead of fabrics has been used to obtain a satisfactory correlation between abrasion-resistance of yarns and of fabrics prepared from these yarns as rated by a standard Taber fabric abrasion test. The yarn-sheet test simplifies the determination of the abrasion-resistance of a yarn type by eliminating the necessity

of fabric preparation. It also removes from abrasion measurements the complicating factor of fabric construction and processing without sacrificing sensitivity or reproducibility. The Taber yarn-sheet abrasion test, like the Taber fabric abrasion test, measures abrasion-resistance alone.

Acknowledgment

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Literature Cited

1. Brown, K. C., Crawshaw, H., and Morton, W. E., *J. Text. Inst.* **22**, T64–76 (1931).
2. Buckley, G. H., and Davis, W. J., *J. Text. Inst.* **25**, T133–40 (1934).
3. Davis, E. H., and Gurney, H. P., *J. Text. Inst.* **23**, T201–10 (1932).
4. Dawson, T. R., *J. Rubber Research* **15**, 65–91 (1946).
5. Fletcher, H. M., *Rayon Text. Mo.* **27**, 78, 88 (1946).
6. Hall, H. S., and Kaswell, E. R., TEXTILE RESEARCH JOURNAL **15**, 178–89 (1945).
7. Hamburger, W. J., TEXTILE RESEARCH JOURNAL **15**, 169–77 (1945).
8. Hamburger, W. J., and Lee, H. N., *Rayon Text. Mo.* **26**, 1–8 (1945).
9. Jaumann, A., *Kunstseide* **21**, 9–16 (1939), abstracted in *J. Text. Inst.* **30**, A261 (1939).
10. Lester, J. H., *J. Text. Inst.* **28**, P209–11 (1937).
11. Matthes, M., and Keworkian, A., *Melliand Textilber.* **24**, 216–18, 249–54 (1943).
12. Schwartz, E. R., *Textile World* **72**, 739, etc. (1927).
13. Skinkle, J. H., *Am. Dyestuff Reptr.* **27**, 109–15 (1938).
14. Tait, J. H., *Rayon Text. Mo.* **26**, 61–2 (1945).
15. Tanenhaus, S. J., and Winston, G., Office of The Quartermaster General, Textile Series—Report No. 45.
16. Walker, A. C., and Olmstead, P. S., TEXTILE RESEARCH JOURNAL **15**, 201–22 (1945).

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Constitutional Factors in the Production of Artificial Protein Fiber*

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Abstract

Recent developments in the chemistry of artificial protein fiber are reviewed, with emphasis on the differences in amino acid content of the various proteins. New experimental results of thermoelastic analysis of protein fibers and determinations of peptide chain length in proteins by end-group analysis are presented.

A DISCUSSION of recent advances in artificial protein fibers—azlons—must necessarily cover almost all the work done in this field, for in the long history of textile fibers these have received serious attention for only about a decade. In this period many millions of pounds of such fibers have been produced, and, more significantly, active research is being carried out today in a large number of laboratories. The early patents and publications on artificial protein fibers were reviewed in 1945 by Peterson, Caldwell, Hipp, Hellbach, and Jackson [63]. In recent years certain investigations have thrown light on the basic chemistry of protein fibers. The Regional Research Laboratories of the Department of Agriculture have emphasized these basic aspects of the problem. This discussion therefore will stress both the published and as yet unpublished work of these Laboratories.

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† One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

The work we intend to describe falls rather naturally into four divisions: (*a*) the internal organization or physical structure of the fiber, (*b*) the chemical composition, (*c*) the reactivity of the constituent groups, and (*d*) studies of chain length in proteins by end-group determinations.

Internal Organization

The concept of an oriented, crystalline structure in fibrous materials was developed primarily in the study of cellulose and synthetic linear polymers. Meyer and Mark [57], Astbury [2], and many others showed that this concept could be applied to the natural protein fibers—silk, wool, and collagen. Therefore, the conversion of a globular protein, edestin from hempseed, to the linear β-keratin structure characteristic of stretched wool by Astbury, Dickinson, and Bailey [4] was a discovery of great interest. They cast films from solutions of edestin in urea and calcium chloride, whose denaturing action on the soluble globular proteins was already known, and, after washing out the reagent, obtained a relatively strong, elastic film which had an x-ray pattern similar to that of unoriented keratin. When this material was stretched 200 to 300 percent an oriented β-keratin pattern was obtained. They considered this to be a demonstration that denaturation involves the liberation of peptide chains which on coagulation aggregate into parallel bundles like those in β-keratin. Later, Lungren and O'Connell [48] produced relatively strong fibers from ovalbumin by spinning a solution of this protein in Nacconol,* an alkyl-aryl sulfonate, into a precipitating bath and subsequently removing the denaturing agent by acetone-water extraction. Senti, Copley, and Nutting [71] showed that these were special cases of a general phenomenon. A number of proteins were crystallized, in the high polymer sense, by moist heat, phenols, acids, alcohols, amides, and other denaturing agents. These crystallites were then oriented by stretching, and a β-keratin pattern with essentially identical spacings resulted in each case. The resultant fibers had appreciably greater tenacity than the unoriented material, and possessed a truly fibrous structure.

Nutting, Halwer, Copley, and Senti [59] made a further valuable contribution by a study of the overall tensile properties—tenacity, stiffness, flexibility, toughness, and elasticity—of both natural and artificial protein fibers as they are related to the molecular configuration. A striking correlation of properties and configuration was found for keratins, silk, collagen, and ovalbumin. Ovalbumin was used as a model of the readily denaturable proteins. The high tenacity of the oriented fibrous form was demonstrated, but unfavorable changes in toughness, flexibility, and stiffness more than offset the advantage gained. Silk fibroin was exceptional in that it had good flexibility in its natural highly ordered state. The low flexibility of oriented ovalbumin was considered to indicate a low effective chain length by analogy with the well-established effect of chain length on flexibility in other high polymers. We therefore reach the provisional conclusion that a highly oriented β-keratin structure possesses a high tenacity but is deficient in other essential properties.

A related but entirely independent approach to the study of the internal organization of fibrous materials has been developed in the study of the long-range elasticity and anomalous thermoelastic properties of rubber. The following discussion is taken essentially from the excellent presentation of Guth, contained in a monograph by the American Association for the Advancement of Science [37].

Most materials we deal with have a low range of elastic behavior—say 0.2 percent. This is consistent with the short distances over which molecular forces operate. As is well known, rubberlike compounds show elasticity over a much greater range. This is the first general characteristic of rubberlike behavior.

A rod of metal, or almost any other solid, elongates when heated, and has less tensile strength. The forces between the atoms or molecules are weakened by the increase of thermal motion. Rubberlike compounds, on the other hand, contract under a given load when heated, or, analogously, require a greater force to hold them at a given extension. Materials which show the latter type of behavior are selenium and sulfur, natural and synthetic rubbers and, under special conditions, cellulose esters and proteins. These materials are dissimilar in many respects; the only common characteristic is that they are all composed of flexible long-chain molecules.

The flexible chain molecules of unstretched rubber are coiled up in disorder, the most probable state. Anyone who has tossed a piece of string into a catch-all drawer can realize the truth of this statement. When rubber is stretched, the chains are necessarily stretched and thus brought into an artificial state of order which is opposed by the internal mobility,

* The mention of commercial products does not imply that they are endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.

or internal Brownian motion. Guth and coworkers showed that these considerations can be extended to the three-dimensional network structure of vulcanized rubber. Flexibility of chains persists in the network of cross-bonded chains. This last point is of importance when we extend these considerations to textile fibers.

It is only reasonable that the tensile properties of any actual high-polymer system should exhibit both types of forces—that is, molecular interaction and internal mobility or entropy effects. Thermodynamical analysis of the forces involved shows there is a close analogy with van der Waals' equation, with its two terms due to interaction and kinetic energy. Where F is the total force, F_u is the internal energy term, and F_s the kinetic mobility or entropy term:

$$F = F_u + F_s;$$

$$F_u = \left(\frac{\delta U}{\delta L}\right)_T;$$

$$F_s = -T\left(\frac{\delta S}{\delta L}\right)_T = T\left(\frac{\delta F}{\delta T}\right)_L.$$

A plot of stress vs. temperature for various elongations gives the second term (F_s) directly,* and this type of analysis can be applied to our system. The value of results which indicate the mechanism by which fibers resist extension is immediately apparent.

But first a word of caution. These ideas neglect the flow or relaxation phenomena so characteristic of fibrous materials. As a practical solution, the fiber is allowed to relax in water under the load until an apparent equilibrium load at each value of L and T is reached. Then a second T is imposed, and the load to give L is determined. Secondly, the effects of swelling on such a system are complex, for swelling is a process dependent on temperature. In fact, Lundgren, Stein, Koorn, and O'Connell [49] have recently used a similar type of analysis to study the interactions between regenerated keratin fibers and water-alcohol mixtures. Nevertheless, the data indicate that these effects, over the temperature range studied, are probably small.

Bull [17] applied thermoelastic analysis to keratin, using human hair as a convenient test material. In general agreement with Astbury's [2, 3] concept of the α-keratin-β-keratin transformation, he found that hair exists in a rather highly ordered state. Extension is resisted primarily by internal energy forces. At low elongations extension is actually favored by entropy forces; only at high elongations do they resist the stress.

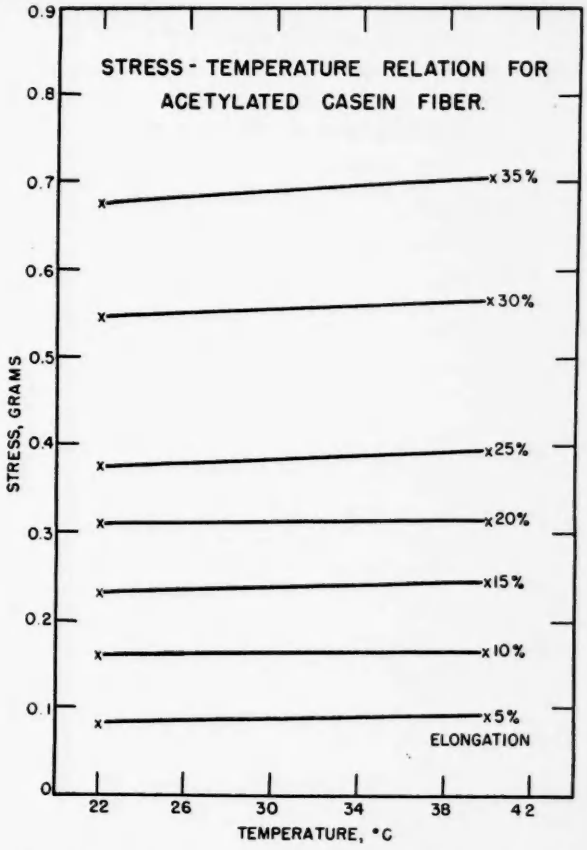


FIG. 1. *Stress-temperature relation for acetylated casein fiber.*

Woods [89] confirmed Bull's results in essence, and showed that as the order in keratin (wool) is destroyed by supercontraction the thermal force becomes of greater importance, and over the initial stages of extension it is large enough to account completely for the load on the fiber. He studied casein fiber, and found that the entropy effect appeared to be much greater than the total load, thus necessitating a negative internal energy. Woods has postulated an internal compression developed by the strong contractile forces as a possible explanation of this anomaly.

We have studied the thermoelastic behavior of our acetylated casein fiber (Figure 1) in the Sookne-Rutherford apparatus [77]. The sample was first relaxed in water at 40°C until the load at definite elongation was reached (about 2 hours). The water

* U = internal energy, L = length, T = temperature in °K, S = entropy. $\left(\frac{\delta F}{\delta T}\right)_L$ is therefore the slope of the line when F is plotted against T at constant L (Figure 1); multiplied by T it equals F_s. F_u is obtained by subtracting F_s from F.

bath was then replaced by one at 22°C, and the load necessary to maintain constant length was determined as soon as the system came to equilibrium (less than 1 minute). The cycle can be repeated several times; it is a fully reversible system under these conditions.

The two components of F were then calculated from the slopes of Figure 1, and these were plotted (Figure 2). The internal mobility term, F_s, is seen to be the dominant force resisting deformation in this fiber up to extensions of 35 percent. This is a demonstration of clearly rubberlike behavior in the wet casein fiber. We did not observe the anomalous hyperentropic effect found by Woods [89].

A third set of considerations, which we cannot directly relate to the internal organization of the fiber but which necessarily is related, was recently developed by Ray [65]. He applied an engineering analysis to the deformations a fiber undergoes in a fabric, and concluded that an individual fiber usually undergoes deformations of not more than 1 or 2 percent. He therefore measured the tensile and torsional properties of fibers within this range, and calculated the work recovery, Young's modulus of elasticity, and the rigidity or torsional modulus. The data were obtained at 70°F and 60 percent relative humidity, and therefore are characteristic of the properties exhibited under normal service conditions.

The results obtained on a series of fibers are of special interest in relation to azlons, for casein fiber closely parallels wool in all these characteristics. We have confirmed the high work recovery, and have demonstrated excellent recovery of length in our continuous-filament casein fiber [64]. Each of the other fibers (viscose, cellulose acetate, fiber A, nylon, silk) differed markedly in one or more factors. All were inferior in work recovery; silk has a high elastic modulus; nylon has a very low rigidity, etc. Further work along this line will be of great interest, for it is probable that fabric qualities such as "hand" and "drape" are the result in large part of the physical properties exhibited at low deformation.

We can therefore conclude that azlon fibers, as typified by casein, are highly elastic. They are composed of flexible chains of undetermined length. The evidence indicates that they possess, at the most, a low degree of internal organization.

Amino Acid Composition

Proteins contain some 15 to 20 amino acids in different proportions. Only in especial cases does one amino acid residue account for more than one-fourth the weight. This heterogeneity of composition distinguishes proteins from other high polymers, which often are derived from a single monomer and seldom contain more than two condensing units. This marked difference between proteins and other high polymers has overshadowed the fact that each protein has a distinctive and characteristic chemical composition.

In recent years the differences in composition of wool and silk have received the attention of several authors [39, 70], but consideration has been given primarily to the ease of packing in a crystalline array. Senti has given an especially lucid presentation of this aspect of the problem [70].

We submit the thesis that each protein does have its chemical individuality. This individuality arises from two factors—the number of side groups of the various types and their arrangement. We have little information about the arrangement of the amino acids beyond the vague conviction that there must be a definite pattern. The fact that they are synthesized in a reproducible manner by plants and animals practically precludes the possibility of a random arrangement. But we cannot go further into this matter here, for it is the basic problem of protein chemistry, and despite our meager knowledge would require close analysis of many bits of collateral data.

The most marked progress in the field in recent years has been in the other aspect of the matter—

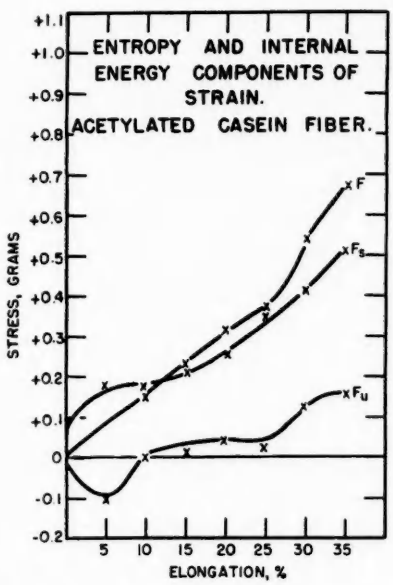


FIG. 2. *Entropy and internal energy components of strain—acetylated casein fiber.*

TABLE I. AMINO ACID CONTENT OF INDUSTRIAL PROTEINS

Amino acid	Side chain	Grams of amino acid per 100 grams of protein					
		Casein	Keratin (wool)	Fibroin (silk)	Zein (corn)	Glycinin (soybean)	Arachin (peanut)
Glycine	Hydrogen	1.90 [73]	6.50 [40]	42.30 [24]	—	0.23 [68]	—
Alanine	Methyl	3.50 [83]	4.40 [40]	24.50 [24]	9.80 [62]	4.12 [68]	4.11 [43]
Valine	Isopropyl	6.02 [83]	4.72 [40]	3.20 [24]	3.98 [42]	4.50 [7]	4.85 [42]
Leucine	Isobutyl	10.55 [83]	11.30 [40]	0.80 [24]	15.40 [12]	8.40 [12]	8.00 [12]
Isoleucine	Sec-butyl	5.27 [83]	—	—	4.30 [9]	4.00 [7]	—
Proline	Trimethylene	10.54 [83]	6.75 [40]	1.50 [5]	9.00 [62]	3.94 [8]	1.37 [43]
Phenylalanine	Benzyl	6.46 [83]	3.75 [40]	1.50 [24]	7.60 [25]	5.30 [8]	2.60 [43]
Aspartic acid	Carboxymethyl	6.70 [6]	7.27 [40]	2.00 [5]	3.40 [45]	3.86 [7]	5.25 [43]
Glutamic acid	2-carboxyethyl	22.03 [6]	15.27 [40]	2.03 [5]	35.60 [13]	19.46 [7]	16.69 [43]
Ammonia (N)	—	1.41 [66]	1.40 [66]	0.00 [24]	3.64 [62]	2.02 [7]	1.67 [43]
Lysine	4-amino butyl	8.25 [50]	3.30 [40]	0.44 [5]	0.00 [62]	5.40 [8]	4.98 [43]
Arginine	3-guanidopropyl	3.94 [50]	10.40 [40]	1.05 [5]	1.60 [85]	5.80 [8]	13.51 [43]
Histidine	Imidazolylmethyl	3.24 [50]	0.70 [40]	0.47 [5]	0.80 [62]	2.30 [8]	1.88 [43]
Serine	Hydroxymethyl	5.87 [66]	9.41 [40]	16.24 [66]	1.00 [69]	6.00 [26]	5.20 [14]
Threonine	1-hydroxyethyl	4.53 [66]	6.76 [40]	1.50 [24]	2.20 [10]	4.00 [7]	2.56 [14]
Tyrosine	Para-hydroxybenzyl	6.28 [47]	5.80 [40]	10.60 [24]	5.90 [31]	4.30 [7]	5.68 [15]
Cystine *	Bis-thiomethyl	0.40 [44]	12.72 [40]	—	0.91 [87]	1.00 [7]	1.51 [14]
Methionine	2-methylthioethyl	3.50 [44]	0.71 [40]	2.59 [5]	2.30 [69]	2.00 [7]	0.67 [14]
Tryptophane	Indolylmethyl	1.37 [22]	0.70 [40]	1.00 [5]	0.20 [69]	1.50 [8]	0.68 [15]
Total		110.35	110.46	111.72	103.99	86.11	79.54

* Cystine + cysteine.

analyses for the amino acids. As recently as 1940 Vickery [86] divided the amino acids into three groups—those about which our information was little more than qualitative; those for which methods of a considerable degree of probable accuracy had been proposed but had not been widely applied; and, lastly, those for which existing analytical methods appeared to be satisfactory and had been widely applied. There were 8, 6, and 9, respectively, in these groups. Since then, whole series of new chemical and microbiological methods [1, 11, 20, 74, 75, 78] have been developed and widely applied, so that

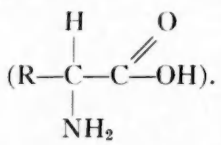
TABLE II. DISTRIBUTION OF AMINO ACID RESIDUES IN PROTEINS

	Moles amino acid residue per 10^5 grams of protein					
	Casein	Keratin (wool)	Fibroin (silk)	Zein (corn)	Glycinin (soybean)	Arachin (peanut)
Nonpolar groups (Gly, Ala, Val, Leu, Ileu, Phe, Pro)	364	344	883	419	248	176
Polar groups						
Amide	101	100	0	260	144	119
Free COOH (diCOOH-amide	99	59	29	8	17	34
Amino (Lys)	56	23	3	0	37	34
Other basic (Arg, His)	44	65	9	15	48	90
Aliphatic OH (Ser, Thr)	94	147	168	28	91	72
Phenolic OH (Tyr)	35	32	59	30	24	31
Others (Cys ½, Met, Try)	27	118	22	26	28	20
Total	456	544	290	367	389	400
Total groups	820	888	1,173	786	637	576
% Nonpolar	45	40	75	55	40	30
% Polar	55	60	25	45	60	70

today essentially complete analyses of many proteins are being carried out [11, 16]. As yet the industrial proteins have been given less attention than the relatively pure and homogeneous proteins such as lactoglobulin of whey, serum albumin, and biologically active enzymes, toxins, antitoxins, and hormones. Casein and its two major components, α- and β-casein, are being carefully investigated in our laboratory [36]. The major seed proteins will probably be studied in the near future.

We have compiled the analytical data on wool, silk, casein, and zein; in each of these proteins the values are good enough for the purpose at hand. The data on wool are taken primarily from the recent compilation of Harris, Mizell, and Fourt [40]. Amino acid analyses of the proteins of soybean, peanut, and cottonseed are not satisfactory. Only about three-quarters of the compositions of these proteins have been accounted for, and new analyses by current methods are greatly needed.

In order that we may consider the amino acid composition from the standpoint of the frequency of reactive groups, we have summarized the structures of the amino acids and the data on each protein, as shown in Tables I and II. In Table I the amino acids are grouped according to the nature of the side group R,



The same data are summarized and expressed as moles per 100,000 grams in Table II. The average residue weight depends on the amino acid distribution in the protein, and ranges from 78 for silk [24] to 119 for casein. The total number of residues per 100,000 grams therefore would be about 1,280 for silk and 920 for casein, if the amino acid content were completely accounted for.

The nonpolar residues vary in bulk, but all are paraffinic or aromatic. Silk and zein contain 75 and 55 percent, respectively, of these nonreactive groups on a molar basis, and the other proteins contain less than 50 percent. It is probable, however, that more satisfactory analyses of arachin and glycinin would show that the nonpolar amino acids actually make up about half the total in these proteins.

The amide group, derived from the second carboxyl group of aspartic and glutamic acid, is the most frequent polar substituent in the plant proteins. Every third residue in zein and every eighth one in casein is an amide. Wool contains about the same number of amide groups as casein, but has a definitely lower content of free carboxy groups. It is probable that a portion of the amide groups of zein could be hydrolyzed selectively, as indicated by the results of Steinhardt and Fugitt [79], so that the relative proportion of carboxy and carboxy amide groups would approach that of wool rather closely. Silk is anomalous in that all its side-chain carboxy groups are free.

The free amino group of lysine is possibly the most reactive side group in a protein. Amino groups are also contributed by the free α-amino group at the end of the protein chain. Since the contribution of these on a weight basis is small, it is omitted in this tabulation (*cf.* page 432). The lysine content ranges from zero in zein to 56 moles/10^5 grams (approximately every fifteenth residue) in casein. Mellon, Korn, and Hoover [54] have shown that the amino group of casein, which constitutes less than 1 percent of the protein on a weight basis, accounts for 25–30 percent of the hygroscopic water sorption. In a second paper it was found that the hysteresis in sorption was not related to this sorption on the amino group, but occurred on other water-sorbing centers [55]. McMeekin has correlated the flexibility of formaldehyde-hardened bristle fibers with the lysine content of the proteins [53]. The strongly basic guanidino group of arginine and the imidazole group of histidine are relatively abundant in the proteins considered except for silk and zein, in which they are only about 1 percent of the total.

The relative frequency of aliphatic hydroxyl groups in all the proteins considered, except zein, is high. These hydroxyl groups arise from serine and threonine. The existence of serine phosphoric acid (phosphoric acid ester of the hydroxyl group) in casein has been demonstrated, and, assuming that all the bound phosphorus of casein (1.6 percent P_2O_5 [88]) occurs as an aliphatic ester, 23 of the 94 hydroxyl groups are conjugated in this manner. The presence of similarly bound phosphorus in the seed proteins has not been demonstrated.

The amount of phenolic hydroxyl group of tyrosine is remarkably constant in these proteins, about 30 residues per 10^5 grams occurring in all except silk, which has about twice as many. Tyrosine is especially interesting in that the photochemical

degradation of silk is related to its tyrosine content [67]. Moreover, the solubility of zein in water at pH 11.4 to 12.5 is thought to be due to the dissociation of the phenolic hydroxyl group [60]. Cystine, methionine, and tryptophane occur in rather small amounts in the seed proteins and casein, totaling no more than 30 residues for the three. In wool, in which the cystine linkages play such an important part, there are 106 such residues out of 888.

No discussion of the polar groups of proteins would be complete if the peptide linkage were not included. It is the most frequently occurring group, one existing for each amino acid in the chain. The polar nature of this group is of importance in solubility phenomena [23], and we have found that a large part of the vapor-phase sorption of water by proteins (45–90 percent) occurs on the peptide linkage [56]. Moreover, the formation of hydrogen bonds between imino hydrogen and carbonyl oxygen of peptide linkages in adjacent chains is thought to be of major importance in stabilizing the native structure of proteins. The only chemical reaction which the peptide linkage can be expected to undergo in fiber production is hydrolysis, and that we make every effort to prevent.

A complete discussion of these data from the standpoint of each individual protein would be redundant, but certain conclusions are brought out by comparisons. When compared on the basis of this tabulation, casein and wool show a rather marked similarity. Casein is a highly polar protein with a large number of free carboxy and amino groups. Wool has a high content of guanidino groups, making the total of basic groups high. The noteworthy difference, to which attention has often been called, is the high cystine content of wool and the extremely low cystine content of casein.

Zein has a distinctive composition. The amide linkage is the only polar group which occurs in large amount. It is almost devoid of acid and basic groups. It has therefore a negligible solubility in water and is soluble in polar organic solvents. Swallen and Danehy [82] have given an excellent discussion of the effect of the various polar groups and of nonpolar solvents on the solubility of zein in mixed solvents. Swallen [81] and Manley and Evans [51] established the solvent properties of an extensive series of binary solvents, all of which contained an alcohol as one component. Later Evans and Manley [29] investigated ternary systems based primarily on water, an alcohol, and an aldehyde, ketone, or nitroparaffin. In these systems the solvent power is correlated with the polar/nonpolar nature of the compounds and their ability to act as hydrogen donors in forming hydrogen bonds. An extensive study of the structure and enzymatic splitting of zein has been carried out by Laine [46].

Silk fibroin is also definitely nonpolar in composition. The only point brought out by the compilation which has not been emphasized before is the high content of aliphatic hydroxyl groups; about every seventh residue has such a substituent. Coleman and Howitt in an outstanding paper [24] have recently reported new chemical and physical data on the structure of silk.

The incompleteness of data on soybean and peanut proteins invalidates any detailed analyses of their amino acid compositions. The nonpolar amino acids were the most difficult to determine before the advent of microbiological methods, and probably the values for this group will be increased when better analyses are available.

In summary, we wish to state again the thesis that each protein has its chemical individuality which arises in the kind and number of its side groups. This fact must be taken into account when we consider the reactions used in producing fiber from industrial proteins. Amino acid determinations of the seed proteins of soybean, peanut, and cottonseed are needed.

Chemical Reactions in Fiber Production

The polar side groups are undoubtedly the primary sites of chemical reaction in the intact protein. There are many possible chemical reactions which can be carried out on these various groups. Two recent reviews of the reactivity of the various groups in native proteins each list over 300 references [41, 61]; hence a thorough review of the subject here is not possible. Therefore, only certain designated reactions which relate to fiber production and properties will be discussed.

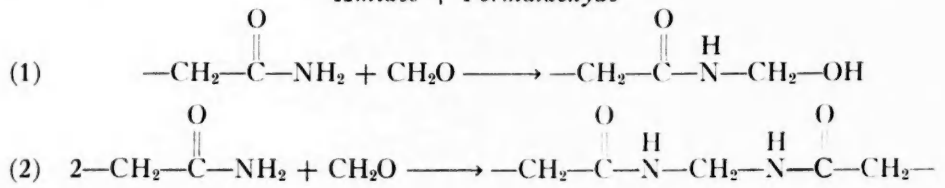
Reaction with formaldehyde to produce a tougher, more flexible material is an essential step in the production of protein fibers. The chemical nature of this reaction has recently been studied with considerable success, and the results merit our attention. Almost all the nitrogen-containing groups in proteins had been considered as possible sites of reaction with formaldehyde, but, with the exception of the free amino groups, the evidence for that was not

good. Wormell and Kaye [90] and Fraenkel-Conrat, Cooper, and Olcott [33] simultaneously recognized that the amount of formaldehyde combined under acid conditions pointed at participation of the amide group, and they brought forward good supporting evidence. The condensation of amides and formaldehyde to methylol amides and even methylene diamides in strongly alkaline solution was demonstrated by Einhorn [28] in 1905, but the conditions used were far from those commonly used in fiber manufacture (Reaction Scheme I).

Fraenkel-Conrat and Olcott have extended their study of the reaction of formaldehyde with proteins to include other possible sites of reaction. They have made excellent use of model compounds, and have evidence of a number of interesting reactions. The complete evaluation of these studies is difficult, for pH, temperature, time, and concentration all affect any particular experiment.

The guanidino group of arginine reacts with formaldehyde under conditions no more severe than those used in treating protein fiber (Reaction Scheme

Amides + Formaldehyde

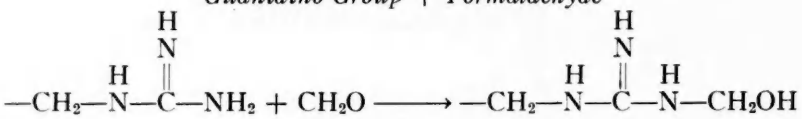


(1) Highly acid conditions, Wormell and Kaye, Fraenkel-Conrat, Cooper, and Olcott

(1) and (2) Highly alkaline conditions, Einhorn

Reaction Scheme I

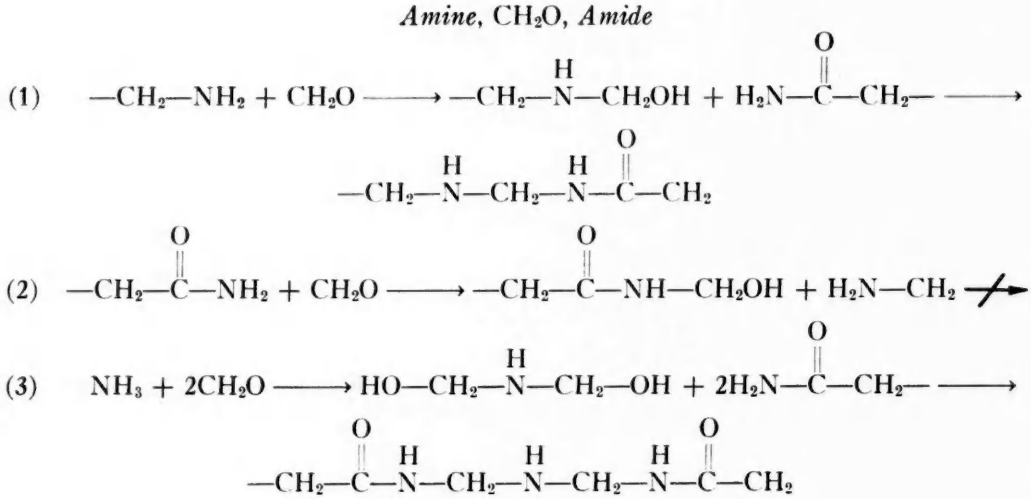
Guanidino Group + Formaldehyde



70°C, pH 3 to 7.6, 4 days

Reaction Scheme II

Amine, CH_2O, *Amide*



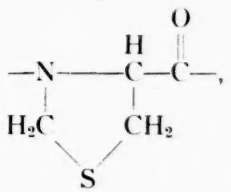
pH 3–8, room temperature, 1 to 4 days

Reaction Scheme III

11). In 4 days, at 70°C and pH 3.0 to 7.6, salmine, a protamine containing about 89 percent of its nitrogen as arginine, combined with more than 1 mole of formaldehyde per guanidyl residue [34].

In an interesting extension of these studies, the reactions of the three-component system amide, formaldehyde, and amine (Reaction Scheme III) have been studied [35]. The rapid reaction in the pH range of 3–8 is the condensation of formaldehyde with primary or secondary amines to form the methylol compound, which then condenses with an amide group. By adding two methylol groups, ammonia or primary amines can condense with two amide groups and thus produce cross-links. The amino methylols also condense with guanidino residues. The peptide bond was not reactive in this system, nor did the amido methylol condense with amino groups under the conditions used.

Direct chemical evidence of the reaction products when wool is treated with formaldehyde to produce shrinkproofness and alkali-resistance has been recently obtained. Middlebrook and Phillips [58] have used chromatographic analysis to demonstrate the production of combined thiazolidine-4-carboxylic acid,



after reaction at pH 1.0, 6.7, and 10.0 at 70–100°C. This reaction is of particular interest, for apparently formaldehyde or its methylol has reacted with the nitrogen of the peptide linkage under neutral and acid conditions. Substitution upon this nitrogen has often been postulated, but except for the biuret reaction, which is carried out in highly alkaline solution, evidence for such reactions has not been obtained.

Wool in which a portion of the cystine had been reduced to cysteine reacted with formaldehyde in two different reactions—one to form combined djenkolic acid, the compound produced when two cysteine residues are combined through a methylene bridge —S—CH_2—S—; the second, that which gave combined thiazolidine-4-carboxylic acid as described above, to give this same compound when it reacted with formaldehyde after reduction to cysteinyl residues.

These studies are of great interest from the standpoint of the protein-formaldehyde reaction, but there is one serious drawback. The reactions discussed so far are reversible; on heating in dilute acid, formaldehyde is evolved, and the groups are set free. The latter conditions are those used in dyeing protein fiber, and all who work in this field have had the experience of seeing a promising fiber go to pieces in the dye bath.

However, nonreversible condensations with formaldehyde also occur [80]. Tryptophane combines with formaldehyde in a stable linkage [32] and with amino methylols, apparently through the >NH group of the ring [35]. The reactive C–H groups of phenols and imidazoles also condense with aminomethylols to produce linkages resistant to acid hydrolysis. These reactions take place with model compounds in neutral or slightly acid conditions, and it appears that the same reactions occur in the reaction of formaldehyde with proteins. The complete evaluation of these reactions will require further extensive study.

Boil stability produced in peanut protein fiber by formaldehyde reaction under drastic conditions of temperature and pH has been demonstrated [30], and we have produced a similar though less pronounced effect on casein fiber. Thus the two lines of attack on the problem—the direct frontal attack and the investigative one—are giving concordant results. It appears probable that this important reaction in protein-fiber chemistry will soon be pretty well understood.

Over the past 5 years we have investigated the effect of a large number of agents on the properties of casein fiber. After the fibers were boiled for an hour in a blank dye bath the results were evaluated primarily on the wet and dry tensile strength and tensile properties. In test after test, none of the reactions appeared to be equal to acetylation with acetic anhydride. This reaction definitely confers boil stability on formaldehyde-hardened fiber. This is a curious result, for it is a monofunctional reagent which has no possibility of producing cross-linkages.

We recently reported results of a silicone treatment of casein fiber [64]. Both wet and dry tensile properties were improved, yet the vapor-phase water take-up was not appreciably affected. We shall not discuss this reaction now, nor the many other stabilizing reactions which we have investigated, for the chemical reactions involved are not well understood. Many of them deserve serious

TABLE III. END-GROUP DETERMINATIONS ON PURIFIED PROTEINS

	Molecular weight	Total amino N (%)	Epsilon amino N (%)	Alpha amino N (%)	Chain weight	Chains per molecule
β-lactoglobulin	35,050 [18] 35,400 [72]	1.260 1.258	1.093	0.167	8,400	4
Bovine serum albumin	70,000 [11]	1.265	1.189	0.076	18,400	4

study, and doubtless the most promising will receive it.

A similar analysis of the participation of the polar side groups in reactions with various inorganic agents is greatly needed. Thus the mode of combination of aluminum, zinc, chromium, and other ions is not at all well understood. The analogy with the use of these metals in tanning leather comes to mind, but there appears to be little clear-cut evidence as to the mechanism of those reactions.

Chain Length by End-Group Determination

The molecular weights of purified proteins are of considerable interest from the standpoint of protein structure, and many have been determined. In a number of cases it has been shown that these molecules in solution can be subdivided by such mild treatment as adding urea, surface-active agents, etc. These agents are believed to break hydrogen bonds which hold native protein structures together. Or these submolecules may be held together by normal covalent bonds. The only bond of this type which has been definitely established is the disulfide bond of cystine. There are other possibilities, such as ester linkage between the carboxy and hydroxy side chains, or peptide-like linkages between carboxy and amino side chains. At present there is no evidence of the existence of these hypothesized linkages in proteins but rather good contributory evidence of their nonexistence. We therefore consider the amino acids to be bound by normal peptide linkages into chains, which may or may not be cross-linked.

How long are these chains? In every field of high-polymer study, chain length has been shown to be of major importance in its effect on physical properties. We have been studying this problem for several years, and do not have a completely satisfactory method as yet. The possibility of cystine cross-linkages makes physical methods such as viscosity, streaming birefringence, and the like of questionable applicability. A chemical method must depend on determination of the free primary carboxyl group at one end of the chain or the free α-amino group at the other end. The best results we have are from determination of the free α-amino nitrogen by difference between the total free amino nitrogen and the epsilon-amino nitrogen calculated from lysine content. Lysine is the only amino acid in these proteins which contributes a second amino group. Rees [66] and Desnuelle and Antonin [26] have shown that hydroxylysine, reported by Van Slyke and associates [84], as a constituent in very low amounts of various proteins, is not present in the proteins which we are studying. Hanke's manometric lysine decarboxylase method [38] has given us excellent results. Our enzyme preparations had a slight arginase content, and corrections for this activity were necessary. Total amino nitrogen was determined by the procedure of Doherty and Ogg [27], which was developed in our laboratory for the analysis of insoluble proteins, but is applicable to soluble proteins as well. The time course of the reaction is determined by successive removal of the gas evolved. After some time—30 minutes to 2 hours—the rate of evolution becomes constant at a low value and remains essentially constant for several hours. Extrapolation of the linear portion back to zero time gives the total amino nitrogen with considerably greater certainty than can be obtained from any arbitrary time of reaction. The free terminal amino nitrogen, however, is the relatively small difference between the two values. The consistency of our results is better than might be expected from such a determination by difference. In Table III are reported determinations on β-lactoglobulin and bovine serum (plasma) albumin. These are purified proteins which have been characterized by a variety of physical and analytical methods. The correlation of our data with the physically determined molecular weights indicates 4 chains per molecule for each protein. The data on β-lactoglobulin agree with those of Brand [11] rather well; he obtained 4.6 units per molecular weight of 42,000. He reported 10 free α-amino groups per mole of 70,000 for bovine serum albumin. Our total amino nitrogen

TABLE IV. CHAIN WEIGHT OF CASEIN

	Total amino N (%)	Epsilon amino N (%)	Alpha amino N (%)	Chain weight	
α-casein	1.00	0.853	0.147	9,500	10,000
	0.99	0.855	0.135	10,400	
β-casein	0.725	0.626	0.099	14,100	14,300
	0.715	0.619	0.096	14,500	
Casein, purified from raw milk	0.94	0.778	0.162	8,600	9,400
	0.92	0.782	0.138	10,100	
Casein, purified commercial	0.929	0.762	0.167	8,400	8,400
	0.928	0.762	0.166	8,400	

value is appreciably lower than the value (1.38 percent) which he reported, and our lysine determination agrees with his. We, therefore, obtain a chain weight of 18,400 and consequently 4 units per mole of 70,000. It must be emphasized that the chain weights determined by these procedures are determined on a weight basis, and are independent of the molecular weight of the protein.

The method has been applied to casein and α- and β-casein, its two major components. Purified casein is composed of about 70 percent α- and 30 percent β-casein. A chain length of 10,000 and 14,000, respectively, was found (Table IV). The purified casein gave a value equal to a chain length of 9,400, obviously not in complete agreement with the value calculated from its two components. A second sample, purified from commercial casein, gave a value of 8,400. The difference between these values of 8,400 and 9,400 is probably not significant, and a value of about 9,000 is indicated for casein. Probably the most reliable molecular weight for comparison is Burk and Greenberg's [19] value of 33,600, determined from the osmotic pressure in urea solution. Again 4 chains per molecule are indicated, but the lack of homogeneity of casein makes such a calculation of questionable value.

We have also applied these method to various seed proteins and to silk fibroin, but the data are only indicative at best. Zein and soybean protein are reported in Table V. The zein was purified from a commercial sample by the procedure of Mason and Palmer [52]. The soybean protein was a commercial protein preparation which may have been contaminated with low-molecular-weight impurities. However, it is probably characteristic of the grade used in much of the experimental spinning work on this protein.

TABLE V. END-GROUP DETERMINATIONS ON SEED PROTEINS

	Total amino N (%)	Epsilon amino N (%)	Alpha amino N (%)	Chain weight
Zein	0.060	0.00	0.060	23,000
	0.061		0.061	
Soybean protein	0.578	0.419	0.159	8,800
	0.562	0.417	0.145	9,600

Zein has been reported to be free of lysine, and we have confirmed this result. Demonstration of the complete absence of an amino acid is difficult, however, and there may be a trace of lysine present as a contaminant. The possible errror from this source probably is not much greater than the error in the lysine determinations of those proteins which have an appreciable content of lysine.

Silk fibroin has been difficult to analyze because it is low in lysine, necessitating a large aliquot for the determination. Our data indicate a rather high chain weight, at least as high as the value of 33,000 obtained by Coleman and Howitt [24] by osmotic-pressure measurements.

The results reported, although not completely satisfactory, indicate that the major industrial proteins have a rather low chain length or degree of polymerization (D.P.). The average amino acid residue weights, calculated from the amino acid compositions, range from about 100 to 120. Thus a chain weight of 10,000 corresponds to a D.P. of 80–100. This is about the minimum for satisfactory physical properties proposed by Carothers and Van Natta [21] for polyesters and by Sookne and Harris [76] for cellulose acetate. The minimum D.P. for acceptable protein fiber is difficult to estimate, for it is possible that the interaction of both the polar backbone and the polar side groups may affect it markedly, and a lower D.P. than that in the analogs discussed above may give good fiber properties. This point has been previously considered by Senti, Copley, and Nutting [71].

It must be emphasized that as yet the chain-weight data reported here can be interpreted only with caution. The length of the chain must be of importance in the physical properties of the proteins as solid bodies, but the probability of cross-linkages and

specific modes of folding make correlations of chain length with properties of proteins in solution dangerous. For example, β-lactoglobulin is relatively symmetric in solution, and casein is asymmetric, yet they have about the same chain weight.

These preliminary results give us hope that we can characterize proteins on the basis of their degree of polymerization and thus make much more satisfactory predictions as to the suitability of a protein for fiber production. It is evident that a complete study of the subject will require intensive work on methods of determination and on preparation of pure proteins for measurement. In seed proteins especially, the latter problem is important. We are working on alternate methods of analyses of end groups and hope to get correlative evidence soon.

Summary

The major points to which we have drawn attention in this paper are:

Proteins are composed of flexible long chains. The manner in which these chains are arranged controls, to a large extent, the properties of fibers produced from them. Each protein has its own chemical individuality, arising from the number and arrangement of the various amino acid residues, and the length of the polypeptide chain. These differences between proteins must be considered in producing fibers from them.

We believe we have demonstrated that research in proteins is extremely active, and that we can expect to describe their behavior much more accurately in the near future.

Literature Cited

1. Archibald, R. M., *Ann. New York Acad. Sci.* **47**, 181 (1946).
2. Astbury, W. T., "Fundamentals of Fibre Structure," London, Eng., Oxford University Press, 1933.
3. Astbury, W. T., *J. Roy. Soc. Arts* **93**, 613 (1945).
4. Astbury, W. T., Dickinson, S., and Bailey, K., *Biochem. J.* **29**, 2351 (1935).
5. Baernstein, Harry D., *J. Biol. Chem.* **122**, 781 (1937).
6. Bailey, K., Chibnall, A. C., Rees, M. W., and Williams, E. F., *Biochem. J.* **37**, 360 (1943).
7. Block, Richard J., and Bolling, Diana, *Arch. Biochem.* **3**, 217 (1943).
8. Block, Richard J., and Bolling, Diana, *J. Am. Dietet. Assoc.* **20**, 69 (1944).
9. Block, Richard J., and Bolling, Diana, "The Amino Acid Composition of Foods," Springfield, Ill., Charles C. Thomas, 1945.
10. Borchers, Raymond, Totter, John R., and Berg, Clarence P., *J. Biol. Chem.* **142**, 697 (1942).
11. Brand, E., *Ann. New York Acad. Sci.* **47**, 187 (1946).
12. Brand, E., Ryan, F. J., and Diskant, E. M., *J. Am. Chem. Soc.* **67**, 1532 (1945).
13. Brazier, M. A. B., *Biochem. J.* **24**, 1188 (1930).
14. Brown, W. L., *J. Biol. Chem.* **142**, 299 (1942).
15. Brown, W. L., *J. Biol. Chem.* **154**, 57 (1944).
16. Buehler, H. J., Schantz, E. J., and Lamanna, C., *J. Biol. Chem.* **169**, 295 (1947).
17. Bull, H. B., *J. Am. Chem. Soc.* **67**, 533 (1945).
18. Bull, H. B., and Currie, B. T., *J. Am. Chem. Soc.* **68**, 742 (1946).
19. Burk, N. F., and Greenberg, D. M., *J. Biol. Chem.* **87**, 197 (1930).
20. Cannan, R. K., *Ann. New York Acad. Sci.* **47**, 135 (1946).
21. Carothers, W. H., and Van Natta, F. J., *J. Am. Chem. Soc.* **55**, 4714 (1933).
22. Chibnall, A. C., *Proc. Roy. Soc. B*, **131**, 136 (1942).
23. Cohn, E. J., and Edsall, J. T., "Proteins, Amino Acids and Peptides" (A.C.S. Monograph No. 90), New York, Reinhold Publishing Corp., 1943.
24. Coleman, D., and Howitt, F. O., *Proc. Roy. Soc. A*, **190**, 145 (1946).
25. Dakin, H. D., *Z. Physiol. Chem.* **130**, 159 (1923).
26. Desnuelle, P., and Antonin, S., *Biochim. et Biophys. Acta* **1**, 50 (1947).
27. Doherty, David G., and Ogg, Clyde L., *Ind. Eng. Chem., Anal. Ed.* **15**, 751 (1943).
28. Einhorn, A., *Ann.* **343**, 207 (1905).
29. Evans, C. D., and Manley, R. H., *Ind. Eng. Chem.* **36**, 408 (1944).
30. Fieldsend, E. C., and Boyes, W. H. D., British Patent 513,910 (Oct. 25, 1939).
31. Folin, O., and Ciocalteu, V., *J. Biol. Chem.* **73**, 627 (1927).
32. Fraenkel-Conrat, H., Brandon, B. A., and Olcott, H. S., *J. Biol. Chem.* **168**, 99 (1947).
33. Fraenkel-Conrat, H., Cooper, M., and Olcott, H. S., *J. Am. Chem. Soc.* **67**, 950 (1945).
34. Fraenkel-Conrat, H., and Olcott, H. S., *J. Am. Chem. Soc.* **68**, 34 (1946).
35. Fraenkel-Conrat, H., and Olcott, H. S. In press.
36. Gordon, W. G., Semmett, W. F., Cable, R. S., and Doherty, D. G., *Federation Proc.* **6**, 255 (1947).
37. Guth, E., in "Surface Chemistry," Washington, D. C., Am. Assoc. Advance. Sci., Pub. No. 21, 1943, p. 103.
38. Hanke, M., *Federation Proc.* **5**, 137 (1946).
39. Harris, M., and Brown, A. E., TEXTILE RESEARCH JOURNAL **17**, 323 (1947).
40. Harris, M., Mizell, L. R., and Fourt, L., *Ind. Eng. Chem.* **34**, 833 (1942).
41. Herriott, R. M., in "Advances in Protein Chemistry," Vol. III, New York, Academic Press, Inc., 1947, p. 169.
42. Horn, M. F., Jones, D. B., and Blum, A. E., *J. Biol. Chem.* **170**, 719 (1947).

43. Johns, C. O., and Jones, D. B., *J. Biol. Chem.* **36**, 491 (1918).
44. Kassell, B., and Brand, E., *J. Biol. Chem.* **125**, 435 (1938).
45. Laine, T., *Suomen Kemistilehti* **12B**, 23 (1939).
46. Laine, T., *Ann. Acad. Sci. Fennicae*, Ser. AII, Chimica No. 11, 7 (1944).
47. Lugg, J. W. H., *Biochem. J.* **32**, 2123 (1938).
48. Lundgren, H. P., and O'Connell, R. A., *Ind. Eng. Chem.* **36**, 370 (1944).
49. Lundgren, H. P., Stein, A. M., Koorn, V. M., and O'Connell, R. A., *J. Phys. & Colloid Chem.* **52**, 180 (1948).
50. MacPherson, H. T., *Biochem. J.* **40**, 470 (1946).
51. Manley, R. H., and Evans, C. D., *Ind. Eng. Chem.* **35**, 661 (1943).
52. Mason, Inez D., and Palmer, Leroy S., *J. Biol. Chem.* **107**, 131 (1934).
53. McMeekin, T. L., *A. S. T. M. Bull.*, No. 125, 19 (Dec. 1943).
54. Mellon, E. F., Korn, A. H., and Hoover, S. R., *J. Am. Chem. Soc.* **69**, 827 (1947).
55. Mellon, E. F., Korn, A. H., and Hoover, S. R., *J. Am. Chem. Soc.* **70**, 1144 (1948).
56. Mellon, E. F., Korn, A. H., and Hoover, S. R., *J. Am. Chem. Soc.*, July, 1948 (in press).
57. Meyer, K. H., and Mark, H., *Ber.* B **61**, 1932 (1928).
58. Middlebrook, W. R., and Phillips, H., *Biochem. J.* **41**, 218 (1947).
59. Nutting, G. C., Halwer, M., Copley, M. J., and Senti, F. R., TEXTILE RESEARCH JOURNAL **16**, 599 (1946).
60. Ofelt, C. W., and Evans, C. D. In press.
61. Olcott, H. S., and Fraenkel-Conrat, H., *Chem. Rev.* **41**, 151 (1947).
62. Osborne, T. B., and Liddle, L. M., *Am. J. Physiol.* **26**, 295 (1910).
63. Peterson, R. F., Caldwell, T. P., Hipp, N. J., Hellbach, R., and Jackson, R. W., *Ind. Eng. Chem.* **37**, 492 (1945).
64. Peterson, R. F., McDowell, R. L., and Hoover, S. R., Paper presented at 112th Meeting, Am. Chem. Soc., New York, Sept., 1947.
65. Ray, L. G., Jr., TEXTILE RESEARCH JOURNAL **17**, 1 (1947).
66. Rees, M. W., *Biochem. J.* **40**, 632 (1946).
67. Rutherford, H. A., and Harris, Milton, *J. Research Natl. Bur. Standards* **27**, 81 (1941).
68. Sasaki, Shuiku, *J. Agr. Chem. Soc. Japan* **11**, 321 (1935).
69. Schmidt, Carl L. A., "Chemistry of the Amino Acids and Proteins," Springfield, Ill., Charles C. Thomas, 1938.
70. Senti, F. R., *Am. Dyestuff Reptr.* **36**, 230 (1947).
71. Senti, F. R., Copley, M. J., and Nutting, G. C., *J. Phys. Chem.* **49**, 192 (1945).
72. Senti, F. R., and Warner, R. C., *J. Am. Chem. Soc.*, Aug., 1948 (in press).
73. Shankman, S., Camien, M. N., and Dunn, M. S., *J. Biol. Chem.* **168**, 51 (1947).
74. Shemin, D., and Foster, G. L., *Ann. New York Acad. Sci.* **47**, 119 (1946).
75. Snell, E. E., *Ann. New York Acad. Sci.* **47**, 161 (1946).
76. Sookne, A. M., and Harris, M., *J. Research Natl. Bur. Standards* **30**, 1 (1943).
77. Sookne, A. M., and Rutherford, H. A., *J. Research Natl. Bur. Standards* **31**, 25 (1943).
78. Stein, W. H., and Moore, S., *Ann. New York Acad. Sci.* **47**, 95 (1946).
79. Steinhardt, J., and Fugitt, C. H., *J. Research Natl. Bur. Standards* **29**, 315 (1942).
80. Swain, A. P., Kokes, E. L., Hipp, N. J., Wood, J. L., and Jackson, R. W., *Ind. Eng. Chem.* **40**, 465 (1948).
81. Swallen, L. C., *Ind. Eng. Chem.* **33**, 394 (1941).
82. Swallen, L. C., and Danehy, J. P., "Zein," in Alexander, J., "Colloid Chemistry," Vol. VI, New York, Reinhold Publishing Corp., 1946, p. 1140.
83. Tristram, G. R., *Biochem. J.* **40**, 721 (1946).
84. Van Slyke, D. D., Hiller, A., and MacFadyen, D. A., *J. Biol. Chem.* **141**, 681 (1941).
85. Vickery, H. B., *J. Biol. Chem.* **132**, 325 (1940).
86. Vickery, H. B., *Ann. New York Acad. Sci.* **41**, 87 (1941).
87. Vickery, H. B., and White, A., *J. Biol. Chem.* **99**, 701 (1933).
88. Warner, R. C., *J. Am. Chem. Soc.* **66**, 1725 (1944).
89. Woods, H. J., *J. Colloid Sci.* **1**, 407 (1946).
90. Wormell, R. L., and Kaye, M. A. G., *J. Soc. Chem. Ind.* **64**, 75 (1945).

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An Application of Spectrophotometry in the Textile Industry: Testing Dyestuff Shipments

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Abstract

Newer spectrophotometric techniques for the absorption measurements of solutions of dyestuffs to determine their strengths are compared to the traditional methods of testing dyestuff shipments by visual appraisal of yarns or fabrics dyed by standard procedures. Sampling errors are measured and discussed in relation to a control-chart method of handling the resultant information. Various examples are cited.

TRADITIONALLY, dyestuff shipments have been tested by visual comparison of yarns or fabrics dyed by standard procedures. This comparison is based on a standard dyestuff mutually accepted by the supplier and user. Certain difficulties are inherent in this type of testing, especially with respect to the time needed per test and the insensitivity of the appraiser to small differences in strength when comparison is made on a single-dyestuff shade.

In some cases, both the consumer and the supplier of dyestuffs are applying measurements made with the General Electric Recording Spectrophotometer to the routine testing of shipments of this type. The theory for the absorption measurement is the well-known application of the Beer-Bouguer-Lambert law [1] to give the strength of a solution of a dyestuff expressed as percent of a standard:

$$\text{Percent strength} = \frac{\log T}{\log T_s} \times 100\%.$$

There have been various descriptions of this application in the literature, including one by Stearns [3] and another by Monego and von Bergen [2].

The control of dyestuffs by absorption measurement on their solutions has certain disadvantages, especially since the depth of shade of the resulting dyed fibers is the variable to be controlled. Differences in substantivity of the dye for the fiber will not be indicated, and errors may result with dyes which are mixtures whose proportions may change somewhat from one shipment to another.

However, allowing for infrequent occurrences of these difficulties, and considering the appreciable amount of time saved and the increased precision obtained as compared to the older method of dyeing each sample, we have found absorption spectrophotometry of great value.

Method

A standard sample of each dyestuff which has been mutually accepted is obtained from each dyestuff supplier. Often those suppliers who use spectrophotometric techniques in standardizing their production lots will supply any supplementary information which they may have on the peculiarities of the particular dyestuff in question. Samples of the standard are then run, according to the procedures described later in this report, to determine the concentration in aqueous solution which is necessary to produce a transmission at the wave length of maximum absorption of about 20 percent.

It is important to note, with respect to the standard dyestuffs, that if the supplier should change some detail of the manufacturing procedure a new standard should be issued to conform to the changed conditions.

The preparation of solutions for test entails the usual volumetric, chemical, analytical technique with the addition of certain precautions. A good outline of these precautions and an indication of their relative importance can be found in Stearn's doctoral thesis [4]. Some of the more common ones are:

1. Type of solvent—usually water for acid and chrome dyes.

2. pH—controlled by weak buffers and distilled water.

CHART I. CHART FOR RECORDING DATA

Dye Name	Color
Mfgr.	Color box no.
Date standard test	Curve no. standard
Buffer to pH	Wave length, max. abs. Mμ
Cell length	Dilution
$-\log T_s$	% Strength = $(-\log T/-\log T_s) \times 100\%$

SHIPMENTS

	Barrel No.	Lot No.	$-\log T$	% Strength	Curve No.
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					

3. Concentration variations which are anomalous with respect to Beer's Law. Usually caused by dyestuff-solvent interaction.

4. Temperature effects—minimized by use of constant-temperature room. The solution heating temperature is also significant.

5. Ageing effects—may be caused by a photochemical process or by some other change.

6. Metal ions—distilled water should be free from metal ions, especially those metals forming lakes with the dyes.

The procedure used in our laboratory is as simple as it is quick. Distilled water is used for all solutions and the temperature to which the initial solution is heated is controlled at 95°C for 1 minute. The solution is buffered to pH 5 for acid dyes and pH 9 for chrome dyes during the dilution procedure, which reduces the concentration used for each dyestuff to that necessary to give approximately 20 percent transmission at the wave length of maximum absorption with a 1-centimeter cell. All solutions are measured within 1 to 4 hours of preparation at the temperature of the room, which is controlled at 70°–75°F. Many dyestuff solutions can be kept much longer, however, with no appreciable changes. In cases of dye-solvent interaction and other undesirable effects, polyethylene oxide condensates of the nonionic type have been reported by Taylor and Simon to be of value [5]. We have not found this necessary, however, with the type of dyes with which we are concerned.

The spectrophotometer used is the standard commercial model with 10-millimicron effective slit width. One-centimeter cells are used with distilled water in the standard side of the absorption chamber. The white reflectance blocks chosen are either magnesium carbonate or matching vitrolite slabs. In either case, if the match is within ± 0.15 percent reflectance, it is considered to be satisfactory.

Calculation and Interpretation of Data

The data for each dyestuff in current usage are placed on a card, which is set up as shown in Chart I. In this way the clerical work involved is minimized and the essential information is concentrated on one simple card.

The strength values so obtained are then plotted on a control chart, one for each type of dyestuff from each particular source. In order to make use of the control-chart technique, however, it is necessary to have information about the precision of the numbers involved with respect to both the measurement and the sampling.

The variations caused by the technique of measurement are relatively small, as indicated by the fact that for five determinations on the same sample the

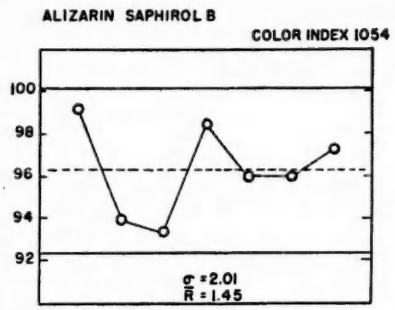

FIG. 1. *Control chart for Alizarin Saphirol B.*

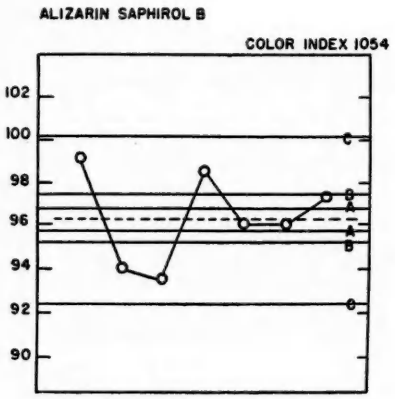

FIG. 2. *Control chart for Alizarin Saphirol B showing various limits.*

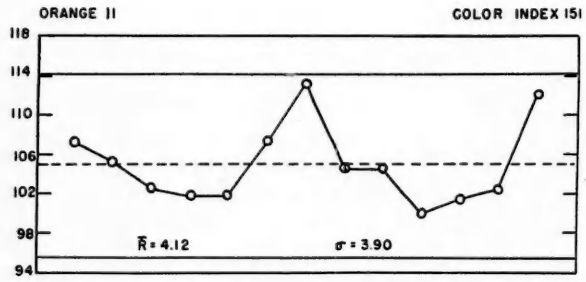

FIG. 3. *Control chart for Orange II showing wide but controlled variation.*

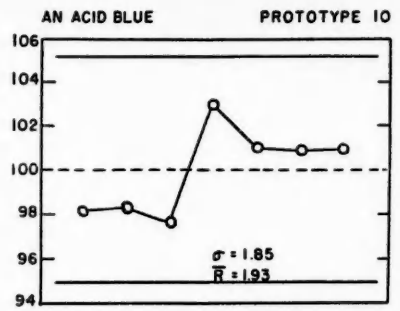

FIG. 4. *Control chart for an acid blue showing close adherence to the standard strength.*

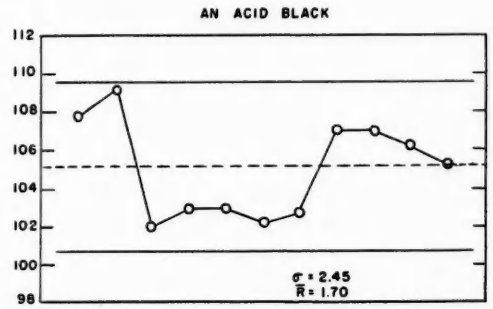

FIG. 5. *Control chart for an acid black which is a mixture of dyestuffs.*

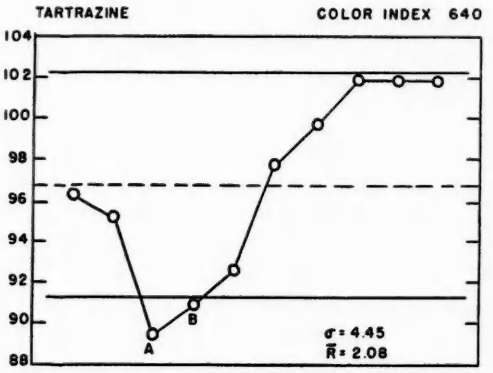

FIG. 6. *Control chart for Tartrazine showing lack of control.*

standard deviation was found to be 0.33 expressed as percent of standard strength. With five different samples taken with a boring tool at different levels in a single shipping container of Orange II, Color Index Number 151, a standard deviation of 0.81 was found, indicating that sampling errors within a container are also small.

However, referring to the control chart for Alizarin Saphirol B, Color Index Number 1054, shown in Figure 1, we see that the standard deviation around the mean value for all shipments measured is approximately 2.0 expressed as percent of standard strength. These facts give rise to a situation in which the method of testing and sampling is much more precise than is required for choosing control limits for a material showing as great a lack of uniformity as that observed. In other words, the variation from one shipment to another is large compared to the variations within a given unit.

It is necessary, then, to be somewhat critical about the choice of limits and about deciding what represents an unsatisfactory shipment in terms of variation

from an accepted standard of strength. Clearly, these limits of acceptability must bear a reasonable relationship to the controllability of the dyeing process to which the results are to be applied. The statistical approach must, therefore, be chosen with full regard for the practical application to be made of the resulting information.

There are at least four essentially different methods of choosing these limits. The first possibility is to base the choice on the maximum variation tolerable before the dyeing results in a commercially inacceptable match. Not only are these limits a function of the shade being dyed, but they are almost impossible to determine because of the variation in wools, and in the actual operation of the dyeing. Furthermore, if one is desirous of improving the reproducibility of the dyeing process, then such limits would not give sufficient control. The remaining three methods are statistical in nature and can be described in relation to the data obtained for Alizarin Saphirol B, previously shown. Figure 2 shows the information for this dyestuff plotted with three different limits. Limits A-A are based on the precision of the measurement, and vary $\pm$ 0.45 from the mean. Limits B-B are calculated from the sampling precision to be about $\pm$ 1.10 percent. Limits based on the observed variation from one sample to another are shown by C-C. They have the value of $\pm$ 3.86, but vary with the particular dyestuff being tested. These limits were calculuated according to the recommendations for control charts of individuals given in the "A.S.T.M. Manual on Quality Control, Section 3—Control Chart Method of Analysis and Presentation of Data," soon to be published. The method is based essentially on the calculation of an average of the ranges of nonoverlapping subgroupings of two values arranged in chronological order. The actual limits can then be calculated from the average range obtained.

A typical example of a control chart for a dyestuff with rather wide but controlled variation is illustrated in Figure 3 for Orange II, Color Index Number 151. A chart for an acid blue, Prototype 10, shows rather close adherence to standard in Figure 4. Blacks and other colors which are mixtures of dyestuffs can also be handled in this way, as indicated by the chart shown in Figure 5 for an acid black which is known to be a mixture of dyestuffs.

Correlation has been obtained between the spectrophotometrically determined strengths and those obtained from sample dyeings. In the control chart in Figure 6 for Tartrazine, Color Index Number 640, samples marked A and B were found to be only 89.2 and 90.9 percent, respectively, of the standard strength. When these two samples were dyed by our previously standard technique of a self-shade of ½ percent based on the weight of the wool, the weakness was visible upon comparison with the standard dyeing. Smaller differences can also be seen, however, if a combination shade is chosen so as to show small differences in yellow as a large visible change.

Summary

The fact that relatively precise determinations of the strength of dyestuffs can be obtained spectrophotometrically brings forth two further consequences when the dyeing process in use is controlled to a proper degree. First, the strengths thus obtained can be used to modify the shade recipes used by the dyer; and, second, the burden will be placed on the dyestuff manufacturers to improve their control to conform with the observed dyeing precision. Obviously the basis for these considerations is the fact that the spectrophotometer can be used to reduce the strength of a given dyestuff shipment to a reasonably precise number.

In conclusion, then, it can be definitely reported that the spectrophotometer is of clear-cut value to an operating textile manufacturer consuming dyestuffs. The testing of shipments with this method not only gives an increased accuracy and precision over the visual examination of dyeings, but it also saves as much as ½ hour per test on the average.

Literature Cited

1. Gibb, T. R. P., "Optical Methods of Chemical Analysis," New York, McGraw-Hill Book Company, Inc., 1942, p. 74.
2. Monego, C., and von Bergen, W., *Am. Dyestuff Reptr.* **32**, 1 (1943).
3. Stearns, E. I., *Am. Dyestuff Reptr.* **33**, 1 (1944).
4. Stearns, E. I., Thesis, Rutgers University, 1945.
5. Taylor, H. H., and Simon, F. T., *Am. Dyestuff Reptr.* **34**, 319 (1945).

Book Reviews

The Heritage of Cotton. Revised Edition. M. D. C. Crawford. New York, Fairchild Publishing Co., 1948. 294 pages. Price, $3.00.

(Reviewed by Earl E. Berkley, National Cotton Council of America)

Rarely does one have the privilege of reading a book that is so well written that facts concerning technical developments become as interesting as events in the lives of his favorite characters. *The Heritage of Cotton* is such a book.

Progress in the cotton industry, throughout the world, is portrayed so well that discrepancies in the descriptions of technical developments do not detract from its value. Interesting and informative conclusions, and even predictions, are convincingly pointed up with statistics on the production, processing, and use of cotton. The human side of the cotton industry, with its poverty, heart-breaking disappointments, and wealth, is also well delineated. The original book was not changed, but there is an addition covering the period since 1924 and some additional historical records. The new portion, entitled "In Retrospect," covers a world of material but could even be expanded to advantage. The impression is given that on the basis of the background covered in the earlier edition the future of textiles can be very dramatic, as great masses of under-privileged people are grasping the power of technical skills.

There are a few of the usual errors of processing and the index does no credit to such a learned work. The excellent illustrations are well reproduced.

Few industries have more artistic appeal than textiles and this treatise points out that many of the outstanding developments were inspired by a love for the beautiful. It is well worth reading and should be a desirable addition to a library.

Imparting Water-Repellency to Textiles by Chemical Methods: An Index of Compounds Used. H. A. Schuyten, J. David Reid, J. W. Weaver, and John G. Frick, Jr. U. S. Department of Agriculture, Bureau of Agricultural and Industrial Chemistry, June 1, 1948. 93 pages. (Processed)

(Reviewed by M. I. Landsberg, Textile Finishing Laboratory, Quartermaster Research and Development Laboratories)

The authors have compiled a comprehensive, noncritical index of compounds normally used as water-repellent agents, as well as the starting materials and intermediates used in their production. This index supplements a review of the literature published under the same title (TEXTILE RESEARCH JOURNAL, this issue, page 396) and is intended to facilitate finding specific references to any of the compounds cited in the literature survey. A total of 332 references are included, 301 of which are patent references.

The compounds are divided into 29 distinct classes and are presented alphabetically. They have been classified primarily according to their functional groups, but are cross-indexed under other headings, depending upon their chemical structure. A compound such as stearylamidomethyl pyridinium chloride, for example, is listed under both "Quaternary Pyridinium Compounds" and "Amides." The number assigned to the original reference is listed after the compound wherever it appears under various classifications. The authors differentiate between prime water-repellent agents and compounds used as intermediates or starting materials.

No attempt is made to indicate the commercial feasibility of compounds listed, the types of fabrics to which they can be applied, or their durability characteristics. Only those products are included which appear to react chemically with the fiber and no mention is made of wax-type compounds.

This index should be of considerable use to organic chemists working in the field of water-repellent synthesis, and to research personnel seeking to improve the water-repellency characteristics of various fibers by physical-chemical means. For mill men interested primarily in production this index can serve only as general background material.

Long Vegetable Fibers. Ludwig Weindling. New York, Columbia University Press, 1947. 311 pages. Price, $5.00.

(Reviewed by Robert B. Evans, Southern Regional Research Laboratory)

Although the long vegetable fibers are overshadowed in economic importance by such fibers as cotton, wool, and rayon, they play a highly important role in both our peacetime and wartime economies, and are the material of very substantial growing and processing industries. Despite this fact, one finds only an occasional reference to the long vegetable fibers in American textile periodicals, and Mr. Weindling's new book, to the best of this reviewer's knowledge, is the first general study on the subject ever to be published in the United States.

The first three chapters of *Long Vegetable Fibers* provide general information on the use and development of these fibers, their characteristics, and on economic aspects of growing and processing them. Next, there are five chapters on the cultivation of Manila hemp, sisal, and other hard fibers; on their marketing, manufacture, and utilization; and on the cordage industry of the United States and Canada. Jute, flax, hemp, sunn hemp, and ramie are similarly treated in the remainder of the book.

This study provides an accurate, diversified treatment of the subject, and from now on undoubtedly will be the point of departure for anyone seeking to learn about long vegetable fibers. Although the book has a good index, it is disappointing to find that sources of information are given only infrequently and that no references are given to other literature on the subject. Mr. Weindling is, nevertheless, to be commended for making this highly valuable addition to textile literature.

Cotton Textile Costs. By Committee on Costs, Frank C. Williams, chairman. New York, The Cotton-Textile Institute, 1948. 95 pages.

(Reviewed by Robert B. Evans, Southern Regional Research Laboratory)

A crusade for scientific cost practices was one of the first activities of the Cotton-Textile Institute after it was founded in 1926. At that time it was found that only 10 percent of the industry was using reasonably effective cost systems. Yet accurate cost accounting is an absolute necessity for control of costs, production planning, maintenance of credit, and price setting—all essential to operation of mills at a profit. Accurate cost records also are needed in connection with wage negotiations, taxes, and tariff matters.

This study, initiated by the Cost Committee of the Cotton-Textile Institute in the closing months of World War II, was prepared mainly by Lewis F. Sawyer. It consists of twelve chapters, one on the essentiality of adequate cost records, eight on methods of keeping accurate cost records, and three final chapters on "Costs for Guidance as to Sales Policies," "Use of Standards in Measuring Cost Variation," and "Reasons for Profits or Losses."

Although this publication will not serve as an all-in-all cost-accounting textbook, it should have considerable value as an auxiliary handbook dealing with the specialized problems of the textile industry. Close attention to actual costs is needed if the industry is to avoid long periods of profitless operation such as it has had in the past.

International Industry Yearbook (1948). Edited by Lloyd J. Hughlett. New York, Kristen-Browne Publishing Co., 1948. 416 pages. Price, $10.00.

(Reviewed by E. R. Schwarz, Massachusetts Institute of Technology)

This is an annual publication—this year of more than 400 pages—well bound and profusely illustrated, by authorities in fields ranging from world industry and industrial research through domestic industry in all its branches. Textile references are to be found directly and indirectly in a number of places. In addition, much of the subject matter of the 27 chapters is of interest to the textile manufacturer, such as that in the fields of air-conditioning, metallurgy, plastics, power, packaging, electronics, illumination, and chemicals.

The chapter on textiles is written by Julian S. Jacobs, Director of Publications for the Textile Research Institute, Inc. This chapter covers economic developments; fibers and their production; advances in processing, finishes, textile education; and research developments. A list of 228 references is of considerable interest and value.

The volume is a most authoritative and useful current reference.

ABSTRACTS

SERVICES AVAILABLE

Reprints of the original articles abstracted in TEXTILE RESEARCH JOURNAL *are often available from the publishers. Otherwise, it may be possible to secure copies of the periodicals. Orders should be sent direct to the publishers.*

Photostat negatives of articles abstracted will be furnished to members of the Institute at a cost of 25 cents per page for pages not exceeding 7 inches in width and 50 cents per page for large sizes up to 11½ x 14 inches. Photostats of patents are 50 cents per page. The library's service charge will be added.

Microfilm copies and paper enlargements of microfilm may be obtained from: Microfilms Inc., 313 N. First St., Ann Arbor, Mich.; New York Public Library, New York N. Y.; Yale University Library, New Haven, Conn.; Harvard University Library, Cambridge, Mass.; and Library of Congress, Washington, D. C. Translations may also be obtained from the above sources.

A list of periodicals abstracted, the abbreviations used in references to articles, and the addresses of publishers of English language publications is given in the January, 1948, issue, page 48.

ANALYSIS: TESTING: LABORATORY METHODS

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Amino Acids

Analytical determination of basic groups in amino acids and proteins. D. P. Grettie. *Science* **106**, 277 (Sept. 19, 1947).

The basic groups of amino acids (except arginine and histidine) or of proteins can be determined by dissolving the sample in 0.05*N* $Ca(NO_3)_2$ solution saturated with $Ca(OH)_2$. The mixture is shaken repeatedly during a 2-hr. interval, filtered, and titrated with HCl. A blank must be run. H. W. Theller

Text. Research J. July 1948

Modified Chromatographic Technique

The quantitative chromatography of silk hydrolyzate. V. M. Mosley and Ralph W. G. Wyckoff. *Science* **105**, 603–4 (June 6, 1947).

The chromatographic technique of Consden, Gordon, and Martin for recognizing the amino acids in a protein hydrolyzate has been modified to provide quantitative data on the amounts of these acids. The results on silk hydrolyzate were generally similar to those obtained by classical methods, except that a high serine content was found, and little, if any, phenylalanine.

H. W. Theller

Text. Research J. July 1948

Dark-Field Electron Microscopy

Dark-field electron microscopy. I. Studies of crystalline substances in dark-field. C. E. Hall. *J. Applied Phys.* **19**, 198–212 (Feb. 1948).

Dark-field images were studied by fixing an aperture system to the object in the electron microscope. The theoretical factors influencing resolution and the resolution obtainable are discussed. Examples of the application of the dark-field method are given. L. P. Witnauer

Text. Research J. July 1948

Photographic Studies

Longitudinal sectioning of cords and fabrics. T. L. W. Bailey, Jr. TEXTILE RESEARCH JOURNAL **17**, 655–63 (Dec. 1947).

A method is described for making longitudinal sections of multi-ply yarns, cords, and fabrics. Photomicrographs are presented to show the alignment of single fibers, yarns, and plies at various planes along a length of the material. The arrangement of yarns and plies is compared in a ZZS- and ZSZ-twisted cord. Longitudinal slices through the thickness of a fabric are presented to show the internal contact of warp and filling yarns. The pictures reduce the interference normally presented by the thickness of the fabric.

Text. Research J. July 1948

Infra-Red Instrumentation

Infra-red instrumentation and techniques. Van Zandt Williams. *Rev. Sci. Instruments* **19**, 135–78 (Mar. 1948).

A review. 210 references.

Text. Research J. July 1948

Window Glass to Withstand High Pressures

Thin glass window to withstand high pressures. Leo Seren. *Rev. Sci. Instruments* **19**, 123 (Feb. 1948).

The preparation of pyrex glass windows of $\frac{1}{8}$ to $\frac{1}{32}$ in. thickness which have been made to withstand pressures as high as 10,000 lbs./sq. in. is described. L. P. Witnauer

Text. Research J. July 1948

Test for Swelling Behavior

An orifice test to evaluate yarns for swelling-type water-resistant fabrics. Herbert O. Smith, Alton

L. Murphy, and Charles F. Goldthwait. TEXTILE RESEARCH JOURNAL **18**, 124–9 (Feb. 1948).

A technique is described for determining the relative closing capacities, largely a reflection of swelling behavior, of fibers in the form of parallel strands of yarn packed tightly in orifices, by observation of the seepage of water through the yarn. The method has been used successfully to predict the performance of cotton yarns for the type of water-resistant fabric whose utility depends largely upon "self-sealing" by swelling. Relatively wide variations in yarn construction have been shown to have little effect on closing capacity, whereas fiber shape and size, as well as swelling properties, have pronounced effects. Authors

Text. Research J. July 1948

X-Ray Intensities

Recovery time of Geiger counters for x-ray intensity measurement. R. Pepisky, P. Jarmotz, H. M. Long and D. Sayre. *Rev. Sci. Instruments* **19**, 51–2 (Jan. 1948).

Using a grid-controlled x-ray tube, the recovery time of a counter used for measurement of x-ray intensities was measured. The method and conditions under which the measurement was made are described.

L. P. Witnauer

Text. Research J. July 1948

Comparison of Scott Fabric Clamps

Effect of clamp design on fabric breaking strength. Warren T. Kelly and Margaret B. Hays. TEXTILE RESEARCH JOURNAL **18**, 130–2 (Feb. 1948).

The strength values of 10 fabrics, determined by the grab and raveled-strip methods and measured with the new Scott 2-in. fabric clamp and the standard 1-in. fabric clamp, were studied. It was found that the 2-in. fabric clamp did not give more accurate results although the number of jaw breaks was reduced 30%. Authors

Text. Research J. July 1948

CHEMICAL AND PHYSICAL RESEARCH

★

Sorption of Sulfuric Acid by Cellulose

Sorption of sulfuric acid dissolved in glacial acetic acid by cellulose. Takeshi Semba, Eiji Yasunaga, and Teikichi Yamada. *J. Soc. Chem. Ind. Japan* **44**, 748–9 (1941) (though *Chem. Abstr.* **42**, 2425*f* (Apr. 10, 1948)).

Cotton linters were dipped in glacial AcOH containing 0.5–4.0% H_2SO_4 at 15°–55°C, and the amount of H_2SO_4 absorbed by the cellulose in each case was determined from the decrease in concentration of H_2SO_4 in the solution. As the duration of dipping increases, the amount of H_2SO_4 absorbed per g. of cellulose, x/m, reaches a maximum and then decreases gradually to an equilibrium value. The value of x/m decreases linearly as the temperature is raised. $x/m = kC^n$, where C is the concentration of H_2SO_4.

Text. Research J. July 1948

Cellulose Chemistry

Unsolved cellulose problems. Emil Heuser. *TAPPI Monograph Ser.* No. **6**, 8–24, discussion 24–74 (1948). **The hemicelluloses.** Louis E. Wise. *Ibid.* 75–85, discussion 85–94. **Structural analysis of the polysaccharides—gums and mucilages.** E. V. White. *Ibid.* 95–106, discussion 106–7. **The proven chemistry of lignin.** F. E. Brauns. *Ibid.* 108–29, discussion 129–32. **Phenolic constituents of wood.** Irwin A. Pearl. *Ibid.* 133–43, discussion 143–5. **Wood tannins.** Edwin S. Flinn. *Ibid.* 146–61, discussion 161–6. **Wood resins.** George C. Harris. *Ibid.* 167–77, discussion 178–81. **Review of natural coloring matters in wood.** Ralph L. Shriner. *Ibid.* 182–215, discussion 215–19. **Structure and synthesis of gymnosperm lignin.** Alfred Russell. *Ibid.* 220–8, discussion 228–34; cf. *C.A.* **42**, 909*a* (through *Chem. Abstr.* **42**, 1733*i* (Mar. 10, 1948)).

These papers are critical reviews of the present state of the various subjects listed and contain suggestions for future research.

Text. Research J. July 1948

Crystallinity of Cellulose

Deformation mechanism of cellulose gels. IV. General relationship between orientation of the crystalline and that of the amorphous portion. P. H. Hermans, J. J. Hermans, D. Vermaas, and A. Weidinger. *J. Polymer Sci.* **3**, 1–9 (Feb. 1948); *cf.* TEXTILE RESEARCH JOURNAL **17**, 230 (Apr. 1947); **18**, 319 (May 1948).

Ten series of model filaments with increasing orientation and swelling degrees ranging between 16 and 1.2 were prepared from 3 viscoses containing 4, 6, and 10.5% cellulose. Their birefringence was measured and their x-ray diagrams taken and quantitatively evaluated in order to determine the over-all orientation of the fiber substance and that of the crystalline portion. It is shown that a general relationship exists between the orientation of the crystallites and that of the entire fiber substance, which is the same in all fibers stretched in the swollen state. When the birefrigence of a filament is known, the orientation factor of its crystallites can be computed without taking an x-ray photograph. From the data, further evidence can be derived that the orientation of the crystallites cannot be accounted for by the theory of affined deformation.

Text. Research J. July 1948 Author

Colloidal Solutions

The effect of size, shape, and flexibility of the solute molecules on the properties of colloidal solutions. Maurice L. Huggins. *J. Phys. & Colloid Chem.* **52**, 248–59 (1948); cf. *J. chim. phys.* **44**, 9 (1947) (through *Chem. Abstr.* **42**, 2156*e* (Apr. 10, 1948)).

Equations are derived for the concentration dependence of the partial molal entropy of the solvent in a dilute solution containing large solute molecules as a function of the size and shape of the solute mole-

cules. Shape constants were evaluated for spherical and rodlike molecules. Certain of the results can be compared with the results reported by Zimm (*C.A.* **40**, 3327[2]). The agreement with the present treatment is satisfactory.

Text. Research J. July 1948

Sulfuric Acid Steep for Cotton

The sulfuric acid steep at elevated temperatures for gray cotton fabrics. R. E. Hudson, Jr., and Howard M. Waddle. TEXTILE RESEARCH JOURNAL **18**, 232–6 (Apr. 1948).

The literature dealing with the effect of sulfuric acid on the constituents of raw cotton fiber has been reviewed. The constituents of starch slasher mixes have been noted. The sulfuric acid steep has been studied at elevated temperatures in the laboratory. Under carefully controlled conditions the sulfuric acid steep may be conducted at elevated temperatures without fiber damage and with a considerable saving in time. Authors

Text. Research J. July 1948

Curling of Hair

Curling of hair under asymmetric stresses. R. Douglas Wright. *Australian J. Sci.* **9**, 187–8 (1947) (through *Chem. Abstr.* **42**, 2299*d* (Apr. 10, 1948)).

The results of studies on the effects of different treatments (immersing in various organic solvents and aqueous solutions, heating under different conditions, and subjecting to the action of acid and alkaline vapors) on the curling and uncurling of hairs supported the view that the physical distortion during curling mainly distorted the thio groups, which reformed when their energy was raised by heating or the presence of free water. It is suggested that the mechanism of such phenomena in hairs may be analogous to that in contractile proteins during shortening and lengthening.

Text. Research J. July 1948

Properties of Macromolecules

Fundamentals of plastic and elastic phenomena in macromolecular materials. R. Houwink. *Mededeel. Rubber-Sticht., Delft*, No. **41**, 20 pp. (1943) (through *Chem. Abstr.* **42**, 1106*g* (Feb. 20, 1948)).

A review with 30 references.

Text. Research J. July 1948

Polyamides

Plastic applications of the superpolyamides. Paul Mingat. *Inds. plastiques* **3**, 322–8 (1947)(through *Chem. Abstr.* **42**, 1758*g* (Mar. 10, 1948)).

A general review of raw materials, special properties of superpolyamides (*I*) ("nylon"), and methods and apparatus for their processing. *I* can be processed by fusion methods (injection, compression molding, extrusion, and casting) and by dispersion (in solvents, swelling agents, and plasticizers). The applications and properties of the various products are described.

Text. Research J. July 1948

Light-Scattering by Polymers

The scattering of light by solutions of polymers. Paul Doty. *J. chim. phys.* **44**, 76–89 (1947) (through *Chem. Abstr.* **42**, 1787*a* (Mar. 20, 1948)).

Molecular-weight, molecular-size, and molecular-shape determinations by light-scattering measurements are reviewed. 35 references.

Text. Research J. July 1948

BLEACHING: DYEING: FINISHING

★

Dyeing Rayon

Dyeing rayon in vat and direct. Anon. *Am. Wool and Cotton Reptr.* **14**, 9, 10, 19 (Apr. 1, 1948).

The practicability and procedures used in dyeing rayon in cake form by vat and direct dyes are outlined.

Text. Research J. July 1948 A. L. Landau

Dyeing Viscose-Acetate Mixtures

Reserve and two-color effects for synthetic fiber mixtures. Wolfgang Brunschmid. *Melliand Textilber.* **28**, 396–8 (1947) (through *Chem. Abstr.* **42**, 2107*d* (Mar. 20, 1948)).

The dyeing of viscose fiber without dyeing acetate fiber, precautions in the use of wooden vats for dyeing, the selection of dyes, the washing of soiled acetate–cellulose fibers, the necessity for immediate drying (without undue delay), after-treatment, the stripping of dyeings with activated charcoal, the dyeing of the acetate cellulose fiber without dyeing the viscose, avoiding irregularities in dyeings, and the dyeing of two-color effects are discussed.

Text. Research J. July 1948

Wool Finishing and Dyeing

Shrinkproofing, dyeing, and finishing men's hosiery of wool and nylon blends. V. T. Hardquist. *Textile Age* **12**, 7, 10, 14, 18, 22 (Apr. 1948).

Recommendations for the chlorination and dyeing of woolen hosiery with respect to the penetration, temperature, and dye selection. The handling of wool and nylon blends is discussed. A. L. Landau

Text. Research J. July 1948

Applications of Dyeing Theory

The application of dyeing theory to dyeing practice. E. B. Abbot, H. Crook, and F. Townsend. *J. Soc. Dyers and Colourists* **63**, 462–8 (Dec. 1947).

The relation of dyeing theory to dyeing practice is critically reviewed under 3 headings. Peters' theory concerning the nature and mechanism of the nylon-acid dye combination is shown to explain and to forecast the practical behavior of acid dyes on nylon. The problems of heavy shades, compatibility of acid dye mixtures, penetration, etc., are related through this theory to the degree of sulfonation of the dye and the affinity of its anion. The

similar mechanism which obtains when dyeing wool with acid dyes and the relative significance from the practical viewpoint of dye basicity and affinity are discussed. The dyeing properties of weathered wool, and of wool treated with acid or alkaline hypochlorite, are shown to depend upon the degree of sulfonation of the acid dyes employed. In the case of cellulose, the relative failure of dyeing theories to provide a satisfactory basis for practical application and development is discussed in relation to the limited significance of dyeing rate and other similar data for direct dyes, and the almost complete lack of theoretical work on vat dyes.
Text. Research J. July 1948 Authors

Softening Agents for Textiles

Application of higher dibasic aliphatic acids. Shichiro Shiina. *J. Soc. Chem. Ind. Japan* **44**, 808–12 (1941).—**I. $(CH_2)_{20}(CO_2H)_2$ and its glyceride as softening agents for textile fibers** (through *Chem. Abstr.* **42**, 2117*i* (Mar. 20, 1948)).

$(CH_2)_{20}(CO_2H)_2$ is obtained from Japan wax, and converted to the glyceride. Alcohol solutions of the acid and the glyceride, respectively, are applied to various fibers. The acid is superior to stearic acid and the glyceride is excellent. **II. Glyceride of two dibasic acids as a softening agent for textile fibers and the simple glyceride as a polishing agent.** A mixture of $(CH_2)_{20}(CO_2H)_2$ and $(CH_2)_{18}(CO_2H)_2$ is easier to obtain from Japan wax than are two acids separately. The glyceride of this mixture is a satisfactory fiber-softening material. The glyceride of $(CH_2)_{18}(CO_2H)_2$ is superior to Japan wax itself as a polishing material for wood furniture and leather products.
Text. Research J. July 1948

Softening agents for textile materials. IV. Sei-ichi Ueno and Mamoru Tsujimura. *J. Soc. Chem. Ind. Japan* **44**, 820–1 (1941); cf. *C.A.* **35**, 4215[2] (through *Chem. Abstr.* **42**, 2111*d* (Mar. 20, 1948)).

Fatty acids, synthetic higher ketones, esters of fatty acids, and waxes were found to be useful softening agents for cotton, rayon, and staple fiber.
Text. Research J. July 1948

Slashing

Slashers and slashing. R. A. Silcox. *Textile Age* **12**, 62–4, 68–70 (Mar. 1948).

The mechanism and operating functions of the stretch control and size vat of the slasher are outlined. Squeeze-roll coverings are discussed.
Text. Research J. July 1948 A. L. Landau

FIBERS: YARNS: FABRICS: MECHANICAL PROCESSES

★

Crimped Rayon Staple

Crimped rayon staple use grows. Anon. *Am. Wool and Cotton Reptr.* **12**, 15–16 (Apr. 15, 1948).

The use of crimped rayon staple is expanding as processing is improved through increased fiber cohesion and a greater loftiness is achieved in the finished fabric.
A. L. Landau
Text. Research J. July 1948

Alginate Rayon

Alginate rayon in waterproof cloths. Anon. *Text. Mercury and Argus* **118**, 565 (Apr. 16, 1948).

Spun seaweed bound around twistless cotton and then dissolved after the double yarn has been woven yields a fabric with unique qualities for lightweight, waterproof women's wear. The fabric is made from single twisted cotton yarn, reverse twisted with the new alginate rayon, which thus becomes a double yarn of untwisted cotton bound spirally with it. A. L. Fiori
Text. Research J. July 1948

Viscose Acetate Blends

"Fifty-fifty" viscose-acetate yarns in dress fabrics. R. Birch. *Textile Manufacturer* **74**, 65 (Feb. 1948).

Fabrics which are composed of yarns made of blends of 50% viscose and 50% acetate yield many interesting finishes. Various effects may be introduced by the use of dyes which will color only one of the fibers. It is posible to dye the fabric and to leave one of the fibers white. Both of the fibers in the blend may be dyed the same color or they may be dyed contrasting colors. A. L. Landau
Text. Research J. July 1948

Vinyon N

The story of "Vinyon N." Anon. *Am. Wool and Cotton Reptr.* **12**, 57–66 (Apr. 15, 1948).

"Vinyon N" does not apply to a single fiber but to a resin which can be made into a number of diversified fibers. The background, proposed uses, and properties and types of the fibers are reviewed. A. L. Landau
Text. Research J. July 1948

Reworkable Waste

Reclamation of reworkable waste. Anon. *Textile Inds.* **112**, 105–6 (Apr. 1948).

A discussion of the various methods of handling reworkable waste and of the percentages of reworkable waste produced at each stage of the spinning process. The value of blending staple lengths is questioned, as tests have shown that the small advantage in reduced costs is outweighed by the trouble encountered with settings, tensions, and twist control.
Text. Research J. July 1948 A. L. Landau

Woolen Carding

Woolen carding. Anon. *Platts Bulletin* **6**, 3–5 (Jan.–Feb. 1948).

A description is given of the 2 systems of removing the web from the doffer; namely, the doffing comb and the roller stripping motion. Opinion is divided with respect to the relative merits of these 2 systems, but when factors conducive to good carding, other than stripping the web from the doffer, are considered, the advantages of the latter method are obvious. Illustrations of the roller stripping motion are shown. L. A. Fiori
Text. Research J. July 1948

Physical Properties of Wool

The physical properties of wool. K. Rachel Makinson. *Australian J. Sci.* **9**, 199–203 (1947) (through *Chem. Abstr.* **42**, 2109*e* (Mar. 20, 1948)).

The warmth of wool in fabric form, its shrinkability and the mechanism of shrinkproofing processes, its elasticity, and other properties are discussed in relation to the physical and chemical structure of the wool fiber. Current theories are reviewed.

Text. Research J. July 1948

Improved Knitwear Designs

Random effects in knitwear. W. Davis. *Text. Mercury and Argus* **118**, 377–8 (Mar. 12, 1948).

Techniques to extend the range of design and color of knitted garments so that full use is made of the design capabilities of both the circular and flat knitting machines are described. Effort is made to escape from the more obvious forms of design, and to offer instead patterns depicting bizarre effects of unregulated random character. Illustrated by 8 designs. L. A. Fiori

Text. Research J. July 1948

Handknitting Yarns

Handknitting wool ranges. Anon. *Fibres* **9**, 151 (Apr. 1948).

Technical and general factors of importance to handknitting yarn spinners in starting new color ranges or augmenting existing ranges of shades are described briefly. Techniques for ascertaining standards for new shades and means for arranging shade cards are given.

Text. Research J. July 1948 L. A. Fiori

Twisting Novelty Yarns

Twisting novelty yarns. H. Botley. *Textile Inds.* **112**, 101–3 (Mar. 1948).

An explanation of the different types of fancy twist yarns and the roller mechanisms necessary to produce them. A. L. Landau

Text. Research J. July 1948

MISCELLANEOUS

★

Boll Weevil Control

Benzene hexachloride and chlordan to control cotton boll weevil. Walter M. Kulash. *J. Econ. Entomol.* **40**, 644–50 (1947); cf. *C.A.* **42**, 1372*h* (through *Chem. Abstr.* **42**, 1697*b* (Mar. 10, 1948)).

In field tests on cotton, dusts containing 1% γ-benzene hexachloride did not check 2nd-brood weevils; dusts containing 5% γ-isomer reduced the infestation considerably. Little residual effect was obtained from the 5% dust, and, if used too heavily, it injured the foliage. In laboratory tests, benzene hexachloride was most effective when the weevils came into actual contact with the dust. Benzene hexachloride dusts, exposed 3 days to room air, lost a considerable part of their effectiveness against the weevils. Liquid formulations of chlordan were apparently more toxic than dust formulations but produced a less-rapid kill. At 2–5% γ-isomer content, benzene hexachloride was more toxic to the weevils than chlordan at 2–5% concentrations.

Text. Research J. July 1948

Electric Cake Drying

Cake drying speeded by high-frequency current. T. H. Story. *Textile World* **98**, 114, 115, 208, 210, 212, 214 (Jan. 1948).

Rayon cake drying by means of high-frequency current is advantageous from the standpoint of quality, owing to the reduction in the mean shrinkage variation from the inside to the outside of the cake. Mean shrinkage variation is reduced from 2% to below 0.4%. Drying time is cut from 3 or 4 days to 30 or 60 min. The cost of high-frequency drying is higher than that for the conventional methods, but this is offset by the improved quality and speed of the system.

A. L. Landau

Text. Research J. July 1948

Properties of Fats and Oils

Inventory of oils and fats. H. K. Dean. *Soap, Perfumery & Cosmetics* **20**, 865–7, 1213–16 (1947); cf. *C.A.* **41**, 2591*d* (through *Chem. Abstr.* **42**, 2117*h* (Mar. 20, 1948)).

The physical and chemical properties of the fats and oils, nutmeg butter, olive, olive kernel, palm, palm kernel, peach kernel, pilchard, raisin seed, rape, ravison (from seeds of a wild variety of *Brassica campestris*), and rice oil are reviewed. Safflower, sardine, seal, sesame, soybean, sunflower, tall, tallow (beef and mutton), teaseed, turtle, walnut, whale, and wheat germ.

Text. Research J. July 1948

Toxicity of Chlorinated Hydrocarbons

Hepato-toxic effects following occupational exposure to Halowax (chlorinated hydrocarbons). Norman Strauss. *Rev. Gastroenterol.* **11**, 381–96 (1944) (through *Chem. Abstr.* **42**, 1678*d* (Mar. 10, 1948)).

Report on one case of acute yellow atrophy of the liver by a 6-mo. exposure to Halowax fumes.

Text. Research J. July 1948

Vacuum Pumps

Vacuum pumping equipment and systems. H. M. Sullivan. *Rev. Sci. Instruments* **19**, 1–15 (Jan. 1948).

Various types of rotary oil-sealed, ejector, and diffusion pumps available today are schematically illustrated and described. The fundamental operating principles and utility are discussed. The method for making theoretical calculations of the conductance of the various connections and speed of evacuation of a vacuum system is outlined. A "portable package type" high-vacuum pumping system equipped with fore pump, holding pump, diffusion pump, refrigerated trap, valves, and gages is shown and discussed.

L. P. Witnauer

Text. Research J. July 1948

Vacuum Valve

High-vacuum valve and seal. L. D. P. King. *Rev. Sci. Instruments* **19**, 83–4 (Feb. 1948).

A simple and compact 2-way valve suitable for high-vacuum work and a method of making a seal are described. The valve design is adaptable to a wide range of port openings. L. P. Witnauer

Text. Research J. July 1948

Color*

The following are authors' abstracts of eight papers which were presented in a symposium on color sponsored by the Inter-Society Color Council at the annual meeting of the Technical Association of the Pulp and Paper Industry, New York City, February, 1947.

The papermaker's interest in color. A. H. Croup. *Paper Trade J.* **125**, 48–9 (Nov. 13, 1947).

The papermaker's interest in color is largely for economic and competitive reasons; uniformity in standard lines reduces wastage and produces good will among customers, ability to produce specialities encourages new trade, and the correct use of color in advertising is essential. A better understanding of color theory, color mixing, color measurement and color harmony will lead to a better color product. Author

Text. Research J. July 1948

The description and specification of color. Ralph M. Evans. *Paper Trade J.* **125**, 49–53 (Nov. 20, 1947).

After a brief description of the way in which seeing an object color involves an object, an illuminant, and an observer, it is shown what form specific problems take when considered in this manner. Two types of problems are considered in some detail to show these differing forms. A summary of the three basic types of colorimetry is included. Author

Text. Research J. July 1948

* A limited supply of reprints of the entire symposium is available from Miss Dorothy Nickerson, Secretary of the Inter-Society Color Council, Box 155, Benjamin Franklin St., Washington 4, D. C.

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Color order systems. Carl E. Foss. *Paper Trade J.* **125**, 149–52 (Dec. 4, 1947).

Three general categories may be considered for the classification of color order systems. One group includes those systems that were developed from color terms alone; another group includes those systems which illustrate the performance of colorants in prescribed combinations or mixtures; and a third group includes those systems which were derived from color mixture data. These distinctions deserve emphasis because casual inspection fails to disclose these importantly different features. Unique sets of descriptive terms are required for each example in each category and although it is often desirable to describe one system in terms of another, this must not be construed to dissolve the fundamental difference between the systems. Ample evidence is at hand regarding the usefulness of existing examples in each group and new systems satisfying certain additional needs are now in the process of development. The evaluation of any color order system requires recognition of the color concepts it illustrates before attention is given to the factors of color range, stability, number, size, and form of the samples as well as the factors of body and surface properties of the samples. The convenience and usefulness of its geometrical arrangement also require attention. Author

Text. Research J. July 1948

Relation of gloss to color. Richard S. Hunter. *Paper Trade J.* **126**, 47–50 (Jan. 8, 1948).

Gloss is a variable which must be considered in addition to color when one is studying the factors of appearance. Traditionally, color is associated with diffuse or pigment reflection whereas gloss is associated with specular or surface reflection. Specularly reflected light is generally nonselective (gray). It may be said to cause a gray component to be added to the colored (pigment) component of reflection in amounts which vary with the gloss and the directions of observation and illumination of any specimen. Thus the color of a specimen tends to vary with the directions in which it is illuminated and viewed. These directions must therefore be standardized in any method for measuring color. Similarly, the geometric conditions of any gloss measurement must be carefully standardized if one is to duplicate the gloss measurements of others. There is not one but several different scales of gloss measurement. Each is used to represent the glossy appearance of a material or group of materials of somewhat similar appearance. Author

Text. Research J. July 1948

Spectrophotometry. Norman F. Barnes. *Paper Trade J.* **125**, 39–47 (Nov. 13, 1947).

The basic conceptions of spectrophotometry are discussed from the standpoint of providing a background for considering the general types of spectrophotometric measuring instruments and the direct application of spectrophotometry in the field of industrial color analysis and control. Methods of illuminating and viewing the sample and their relation to the color-measuring problem are included as well as the laws of absorption of dyes and the types and application of various recording scales, such as percent reflection, density, log density, etc. Qualitative identification of the component materials and quantitative analysis of spectrophotometric data provide means of color investigations, color matching, and the standardization of constituent materials and the final product. Author

Text. Research J. July 1948

The I.C.I. standard observer and coordinate system and their use in studies of the color of paper. J. A. Van den Akker. *Paper Trade J.* **125**, 49–54 (July 10, 1947).

Spectrophotometric data in the form of spectral reflectance curves ("color curves") are most useful in connection with mill control of color and in fundamental studies of color. However, it is sometimes necessary or desirable to obtain accurate numerical expression of the color, or of a color difference, corresponding to a color curve or pair of curves. An objective and accurate psychophysical bridge between purely physical data and color sensation is afforded by the I.C.I. standard observer and coordinate system. The I.C.I. system is described with particular reference to reflecting bodies (such as paper) and transparent bodies. Some applications of the I.C.I. system to problems in the paper industry are discussed. Author

Text. Research J. July 1948

Interrelation of color specifications. Dorothy Nickerson. *Paper Trade J.* **125**, 153–71 (Nov. 6, 1947).

The interrelation of color specifications for standard reference material is discussed in three sections. Section 1 relates to various ways of graphing or transforming I.C.I. data: (x, y)—diagram; Judd U.C.S. diagram (1932–5); MacAdam U.C.S. diagram (1937); Breckenridge and Schaub rectilinear U.C.S. (1939); Scofield (1940); Adams (1940); Moon and Spencer (1943); Saunderson and Milner (1944). Section 2 lists several sets of standard reference material by which conversions may be made, or for which data into terms of specifications recommended in ASA-Z44 standard are available in whole or in part: Dominant wave length—purity; Munsell; ISCC-NBS; Ostwald; TCCA standards; Maerz and Paul *Color Dictionary*; Ridgway; Lovibond glasses; Wratten filters. Section 3 reviews the problem of color tolerance specification as it relates to interrelation of color specifications and includes a summary table of formulas developed for tolerance work. Author

Text. Research J. July 1948

Color engineering. Frederic H. Rahr. *Paper Trade J.* **125**, 37–9 (Sept. 4, 1947).

This paper deals with the commercial significance of color engineering, outlining the scope of activity and some representative problems, their analysis, and method of approach to their solution. The results are interpreted in terms of specific accomplishments, together with a review of the growing importance of color and its application. Author

Text. Research J. July 1948